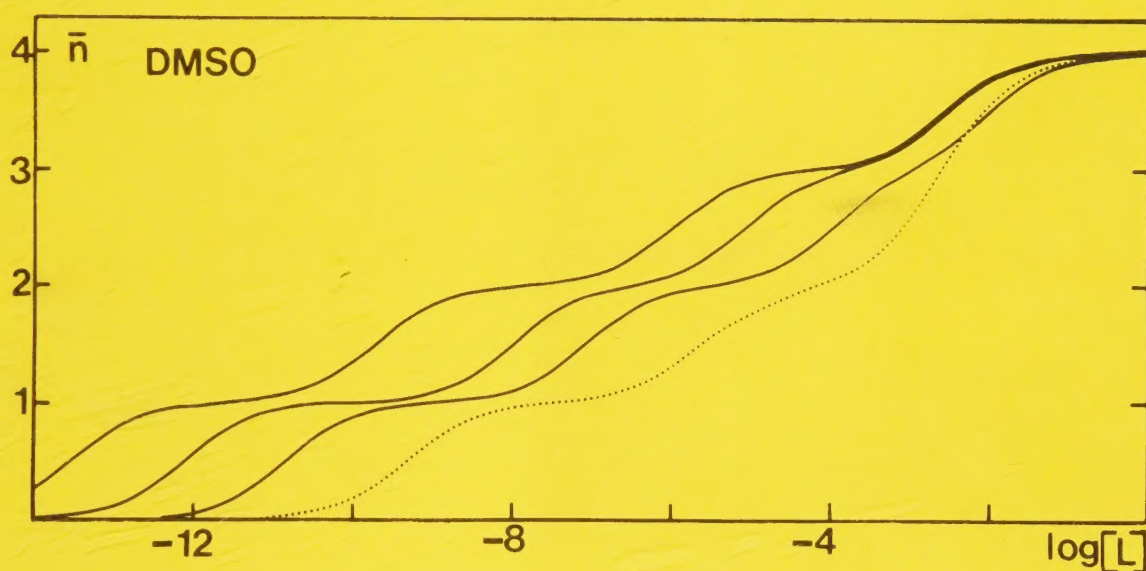


THERMODYNAMIC AND STRUCTURAL STUDIES OF SOME METAL HALIDE AND THIOCYANATE COMPLEXES IN DIMETHYLSULFOXIDE SOLUTION

Ingmar Persson



Lund 1980

Digitized by the Internet Archive
in 2026

THERMODYNAMIC AND STRUCTURAL STUDIES OF SOME METAL HALIDE
AND THIOCYANATE COMPLEXES IN DIMETHYLSULFOXIDE SOLUTION

AVHANDLING FÖR FILOSOFIE DOKTORSEXAMEN

Avhandlingen kommer att försvaras vid offentlig disputation
å Kemicentrum, hörsal F, fredagen den 21 mars 1980, kl 10.15

av

Ingmar Persson
Fil.kand., Ld.

THE UNIVERSITY OF LEIDEN
LIBRARY

UNIVERSITY OF LEIDEN LIBRARY



UNIVERSITY OF LEIDEN LIBRARY
UNIVERSITY OF LEIDEN LIBRARY

UNIVERSITY OF LEIDEN
LIBRARY

Organization
LUND UNIVERSITY

Document name
DOCTORAL DISSERTATION

Date of issue
March 1980

CODEN:
LUNKDL/(NK00-1003) /001-048/1980

University of Lund,
Inorganic Chemistry 1

Author(s)
Ingmar Persson

Sponsoring organization

Title and subtitle

Thermodynamic and structural studies of some metal halide and thiocyanate complexes in dimethylsulfoxide solution

Abstract

The complex formation of the zinc(II), cadmium(II) and mercury(II) chloride, bromide, iodide and thiocyanate systems in dimethylsulfoxide (DMSO) solution have been studied by means of potentiometric, calorimetric, raman and infrared spectro-photometric and x-ray diffraction measurements. Standard electrode potentials for some metal redox systems in DMSO with the $\text{Ag(s)}/\text{Ag}^+$ electrode in aqueous solution as standard electrode have been determined. The thermodynamics of the mercury(II) halide and thiocyanate systems differ markedly between aqueous and DMSO solution. In DMSO, these systems form four mononuclear complexes which are all, except $\text{Hg}(\text{SCN})_3^-$, dominating almost completely in their ranges of existence. The first complex is strongly entropy stabilized. In more concentrated solutions $C_m \gtrsim 0.2 \text{ M}$, it disproportionates into $\text{Hg}(\text{DMSO})_6^{2+}$ and HgX_2 or, in the case of iodide, into HgI_2 and Hg_2I_3^+ . The structures of the DMSO solvated zinc(II), cadmium(II) and mercury(II) ions have been determined both in DMSO solution and solid state by means of x-diffraction measurements. The zinc(II), cadmium(II) and mercury(II) ions coordinate DMSO via the oxygen atoms, as can also be concluded from their raman spectra. Thermodynamics studies of zinc(II), cadmium(II) and mercury(II) halide systems in 1 M and 0.1 M ammonium perchlorate solutions and in other perchlorate media have been performed. Structure determinations of the mode of thiocyanate coordination shows that zinc(II) is coordinated via the nitrogen atom, while cadmium(II) and mercury(II) are coordinated via the sulfur atom.

Key words

Classification system and/or index terms (if any)

Supplementary bibliographical information

Language
English

ISSN and key title

ISBN

Recipient's notes

Number of pages

Price

Security classification

Distribution by (name and address)

I, the undersigned, being the copyright owner of the abstract of the above-mentioned dissertation, hereby grant to all reference sources permission to publish and disseminate the abstract of the above-mentioned dissertation.

Signature _____

Date _____

THERMODYNAMIC AND STRUCTURAL STUDIES OF SOME METAL HALIDE
AND THIOCYANATE COMPLEXES IN DIMETHYLSULFOXIDE SOLUTION

INGMAR PERSSON

LUND 1980

Persson, I. (1980)

Thesis, Inorganic Chemistry 1

Chemical Center, University of Lund

P.O. Box 740, S-220 07 Lund 7, Sweden

This dissertation consists of a review, summarizing the results from the following papers. The papers will be referred to by their roman numerals.

- I. Ahrland, S. and Persson, I.
Standard Electrode Potentials in Dimethylsulfoxide Solution and Solvent Exchange Reactions between Dimethylsulfoxide and Water Involving Metal Ions of Groups IB and IIB.
Acta Chem. Scand. To be published.
- II. Ahrland, S., Persson, I. and Portanova, R.
Equilibrium and Entahlp Measurements on the Mercury(II) Chloride, Bromide, Iodide and Thiocyanate Systems.
Acta Chem. Scand. To be published.
- III. Ahrland, S., Björk, N.O. and Persson, I.
Equilibrium and Enthalpy Measurements on Halide Systems of Zinc(II), Cadmium(II) and Mercury(II) in 0.1 M Ammonium Perchlorate.
Acta Chem. Scand. To be published.
- IV. Ahrland, S. and Persson, I.
Calorimetric Measurements on the Zinc(II) and Cadmium(II) Bromide Systems in Various Ionic Media.
Acta Chem. Scand. To be published.
- V. Sandström, M., Persson, I. and Ahrland, S.
On the Coordination around Mercury(II), Cadmium(II) and Zinc(II) in Dimethylsulfoxide and Aqueous Solutions. An X-ray Diffraction, Raman and Infrared Investigation.
Acta Chem. Scand. A32 (1978) 607.
- VI. Persson, I.
The Structure of Hexakis(dimethylsulfoxide)zinc(II) Perchlorate and of the Hexakis(dimethylsulfoxide)zinc(II) Ion in Dimethylsulfoxide Solution.
Acta Chem. Scand. To be published.

- VII. Sandström, M. and Persson, I.
Crystal and Molecular Structure of Hexakis(dimethylsulfoxide)mercury(II) Perchlorate, $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$.
Acta Chem. Scand. A32 (1978) 95.
- VIII. Ahrlund, S., Hansson, E., Iverfeldt, Å. and Persson, I.
An X-ray Diffraction and Raman Study of Mercury(II) Chloride, Bromide and Iodide Complexes in Dimethylsulfoxide Solution.
Acta Chem. Scand. To be published.
- IX. Persson, I., Iverfeldt, Å. and Ahrlund, S.
An X-ray Diffraction and Raman Study of Mercury(II), Cadmium(II) and Zinc(II) Thiocyanate Complexes in Dimethylsulfoxide Solution.
Acta Chem. Scand. To be published.

CONTENTS

1.	INTRODUCTION	6
1.1.	Background	6
1.2.	Systematization of equilibrium data	7
1.3.	The chemistry of hard and soft acceptors and donors	8
1.4.	Selections of solvent and complex systems	9
2.	EXPERIMENTAL METHODS	14
2.1.	Potentiometric measurements	14
2.2.	Calorimetric measurements	15
2.3.	Raman and infrared measurements	15
2.4.	X-ray diffraction measurements on solids	16
2.5.	X-ray diffraction measurements on solutions	16
3.	CALCULATIONS	17
3.1.	Calculations in the thermodynamic measurements	17
3.2.	Calculations for structure determinations of solids	18
3.3.	Calculations for structure determinations in solutions	18
4.	RESULTS	20
4.1.	Standard Electrode Potentials in dimethylsulfoxide solution	20
4.2.	Solvate exchange reactions between dimethylsulfoxide and water	20
4.3.	Stability constants and thermodynamic functions	22
4.3.1.	The mercury(II) halide and thiocyanate systems in 1 M ammonium perchlorate	22
4.3.2.	The zinc(II) bromide, cadmium(II) chloride, bromide, iodide and mercury(II) bromide systems in 0.1 M ammonium perchlorate	22
4.3.3.	The zinc(II) and cadmium(II) bromide systems in various perchlorate media	27
4.4.	The structure of crystalline zinc(II) and mercury(II) DMSO solvate	27

4.5.	The structures of complexes formed in dimethylsulfoxide solution	29
4.5.1.	The zinc(II), cadmium(II) and mercury(II) DMSO solvates	29
4.5.2.	The mercury(II) chloride, bromide and iodide complexes	30
4.5.3.	The mercury(II), cadmium(II) and zinc(II) thiocyanate complexes	32
5.	DISCUSSION	34
5.1.	Introduction	34
5.2.	Thermodynamics and structures of mercury(II) halide and thiocyanate complexes in dimethylsulfoxide solution	35
5.3.	The influence of medium ions and the ionic strength on the complex formation in dimethylsulfoxide solution	38
5.4.	The mode of coordination of the thiocyanate ion to zinc(II), cadmium(II) and mercury(II) in dimethylsulfoxide solution	39
6.	ACKNOWLEDGEMENTS	40
7.	REFERENCES	41

1. INTRODUCTION

1.1. Background

For the studies of complex formation in solution different methods are needed, both traditional and more recent ones. To elucidate the processes taking place both the thermodynamics and the structures of the complexes should preferably be known. Complex formation reactions in aqueous solution have been studied since many years. The determination of stability constants have been performed by several different methods, for example central ion, pH, solubility and spectrophotometric measurements. To determine the complete thermodynamics, the enthalpy changes of the complex formation must also be determined. This is most precisely and accurately done calorimetrically. Indirect methods should generally not be used as the errors very often are unacceptably high.

During recent years complex formation reaction have also been studied in other solvents than water. Water is in fact a solvent with rather particular properties. Because of intermolecular hydrogen bonding, it possesses a high structural order. Hydrogen bonding is also the reason that certain ligands, as for example fluoride and chloride, are particularly strongly solvated in water. As a consequence, complexes of such ligands are weaker in a protic solvent as water, than in aprotic solvents, where no hydrogen bonds are possible.

Other important information about the complex formation is obtained from the structures of the metal ion solvates and the complexes formed in solution. These structures are determined by high angle x-ray diffraction measurements on concentrated solutions.

By raman and infrared spectrophotometric measurements the mode of coordination if ambident ligands and the bonds strengths in complexes are determined.

By combining the results obtained by the different methods, it is possible to get a detailed picture of the events taking place during the complex formation.

1.2. Systematization of equilibrium data

One important task in solution chemistry has been to determine the composition and stability of metal complexes in solution, primarily in aqueous solution, where a large amount of data has been collected during the years.¹

Ahrland, Chatt and Davies have systemized these data, classifying the acceptors according to their relative affinities for ligand atoms of the same groups.² Two classes exist, viz (a), forming their most stable complexes with the first ligand atom in each group and (b) forming their most stable complexes with a heavier ligand atom in each group. The acceptor classes are characterized by the following affinity sequences of the donor atoms:

class (a)	class (b)
F >> Cl > Br > I	F << Cl < Br < I
O >> S > Se > Te	O << S ≈ Se ≈ Te
N >> P > As > Sb > Bi	N << P > As > Sb > Bi

Pearson has extended this classification to acceptors other than metal ions, and introduced the designation hard for class (a) and soft for class (b), referring to low and high polarizability, respectively, of the acceptor.³ It should be noted however, that a high polarizability is not enough to constitute a (b)-acceptor, rather it is a combination of high polarizability and many d-electrons.^{4, 5} Pearson has also analogously classified the donors as hard and soft ones.⁶ The hard donors are characterized by high electronegativity, low polarizability and they are difficult to oxidize. The soft donors are characterized by low electronegativity, high polarizability and they are easy to oxidize. Generally, acceptors and donors of the same classes form strong complexes, while the complex formation between acceptors and donors of different classes is generally weak. Thus, hard acceptors prefer hard donors and soft acceptors soft donors.⁶



1.3 The chemistry of hard and soft acceptors and donors

The interaction between hard acceptors and donors is mainly electrostatic, and between soft acceptors and donors mainly covalent, involving a true exchange of electrons between the acceptor and the donor.⁷ When the stability constants, β_j , are high, the free energy gains, $\Delta G_{\beta_j}^\circ$ are very negative according to the relationship $RT \ln \beta_j = -\Delta G_{\beta_j}^\circ$. The stability constants and the free energy changes of a complex formation are governed by both enthalpy changes, ΔH° , and entropy changes, ΔS° , according to the formula $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

Strong complexes are consequently formed if the value of ΔH° is very negative, thus if the reactions are strongly exothermic and/or if the value of ΔS° is very positive. Information about the nature of the bonds formed will essentially come from the sign and magnitude of the enthalpy change. Distinctly positive enthalpy changes indicate mainly electrostatic bonds, and negative enthalpy changes mainly covalent bonds. For enthalpy changes around zero the bonds are neither typically electrostatic nor typically covalent. The entropy changes give essential information about the desolvation occurring for each step of the complex formation. One purpose of this investigation has been to study how these functions vary when complexes are formed between divalent d¹⁰ metal ions and halide ions.^{II, 8-11} Especially interesting are comparisons of the entropy changes with the structures of the complexes involved.^{V, VI, 12-15} The complex formation evidently depends very much on the solvation of the reacting species which in turn depends on the solvent used.

In a protic solvent, such as water, the hard ligands are selectively solvated by hydrogen bonding, while the soft ligands are only weakly solvated. In an aprotic solvent as dimethylsulfoxide (DMSO), on the other hand, hydrogen bonding is not possible, and the solvation of hard ligands is therefore markedly weaker. The DMSO solvation of soft ligands are of same magnitude as in water or stronger.¹⁶ The metal ions in this investigation have higher solvation enthalpies in DMSO than in water.^{17, 18} This means that hard ligands are able to form stronger complexes in DMSO than in

aqueous solution, while soft ligands form complexes of much the same strength in water and DMSO. Consequently halide complexes are favoured in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ when going from a protic to an aprotic solvent.

1.4. Selection of solvent and complex systems

This investigation is a continuation of that initiated by Åhrland and Björk.¹⁹ They mainly studied the complex formation of the d^{10} acceptors Zn^{2+} and Cd^{2+} with the halide and thiocyanate ions. The halides provide a suitable series of ligands for a comparison of the solvent influence on the complex formation in protic and aprotic solvents. In this series the hydrogen bonding properties are weaker the heavier the halide ion. The thiocyanate ion behaves in this respect similar to the iodide ion. Thiocyanate is an ambident ligand, able to coordinate both through the sulfur and the nitrogen atom. Consequently, it is able to form complexes with acceptors of different bonding characteristics. Hard acceptors prefer bonding through the nitrogen atom and soft acceptors through the sulfur atom.

The aprotic solvent chosen by Åhrland and Björk was dimethylsulfoxide (DMSO). DMSO is also an ambident ligand, the coordination may occur either through the oxygen or the sulfur atom. Earlier infrared spectroscopic and structural measurements have indicated that all metals, except palladium, platinum, iridium and ruthenium coordinate DMSO through its oxygen atom,^{20, 21}

Table 1. The S-O distance in DMSO is shorter in sulfur coordinated complexes than in free DMSO⁶⁰, while it is longer in oxygen coordinated complexes. Consequently the S-O stretch frequency in infrared increases in DMSO complexes coordinated via sulfur, while it decreases in DMSO complexes coordinated via oxygen. The S-C bond distances decrease in all metal DMSO complexes, and accordingly the S-C stretch frequencies increase. It shall be noted that the M-O-S angle in all complexes coordinated via oxygen is around 125° . This is certainly due to the hybridization of the oxygen in DMSO.

Table 1. Metal - DMSO bond and intradimethylsulfoxide distances (Å) in some metal DMSO complexes.

Compound	M-S distance (Å)	M-O distance (Å)	M-O-S angle(deg.)	S-O distance (Å)	S-C distance (Å)	Ref
S-bonded:						
[Ru(DMSO)(NH ₃) ₅](PF ₆) ₂	2.19			1.51	1.81, 1.82	22
Ru(DMSO) ₄ Cl ₂	2.26, 2.28 2.24-2.26			1.48	1.78-1.81	23
Ru(DMSO) ₃ Cl ₃	2.25, 2.26			1.48-1.50	1.78-1.86	24
[Ru(DMSO) ₆](BF ₄) ₂	2.24-2.26	2.12-2.14		1.47-1.49 ^b , 1.52-1.56 ^c	1.75-1.80	124
Na[Rh(DMSO) ₂ Cl ₄]	2.22, 2.36			1.47	1.90	25
Pd(NO ₃) ₂ ·2DMSO	2.23, 2.25					26
Pd(DMSO) ₂ Cl ₂	2.29			1.48	1.78	27
Ir(C ₁₅ H ₁₃ O)Cl ₂ ·2DMSO	2.24			1.44, 1.46	1.80, 1.82, 1.85	28
Pt(DMSO)Cl ₂	2.23, 2.24			1.45, 1.47	1.77-1.79	29
Pt(DMSO)(NH ₃)Cl ₂	2.19			1.49	1.77	30
Pt(DMSO)(cytidine)Cl ₂	2.20			1.48	1.79	31
cis-Pt(DMSO)(2-picoline)Cl ₂	2.20			1.47	1.78, 1.80	32
transPt(DMSO)(2-picoline)Cl ₂	2.21			1.44	1.79, 1.80	33
K[Pt(DMSO)Cl ₃]	2.19			1.48	1.78	34
O-bridged:						
AgClO ₄ ·2DMSO		2.35, 2.36, 2.49, 2.50		1.50, 1.51	1.78, 1.80, 1.81	35
Hg(ClO ₄) ₂ ·4DMSO		2.37-2.54, 2.13-2.40 ^a		1.40-1.69	1.54-1.90	36
3HgCl ₂ ·2DMSO		2.52, 2.56	121.9, 130.2	1.54	1.78	37

Compound	M-S distance (Å)	M-O distance (Å)	M-O-S angle(deg.)	S-O distance (Å)	S-C distance (Å)	Ref
O-bonded:						
Fe(DMSO) ₂ Cl ₃	2.01		124.5	1.54	1.80	38
Cu(DMSO) ₂ Cl ₂	1.96		118.2	1.53	1.77	39
[Cu(DMSO)(C ₅ H ₅ NO)Cl ₂] ₂	2.28			1.55	1.82, 1.84	41
[Zn(DMSO) ₆](ClO ₄) ₂	2.10, 2.12		119.9	1.49	1.75-1.82	VI
[RuBr ₂ (NO)(DESO) ₂]Br	2.05		123.9	1.54	1.82, 1.83	42
[Cd(DMSO) ₆](ClO ₄) ₂	2.26		121-131	1.52-1.57	1.74-1.80	43
SnCl ₄ (DMSO) ₂				1.51, 1.54		44
Sn(CH ₃) ₂ Br ₂ (DMSO) ₂	2.27, 2.31		119.0, 125.2	1.56, 1.58	1.77-1.82	45
Sn(C ₆ H ₅) ₂ Cl ₂ (DMSO) ₂	2.28, 2.30		126.5, 142.0	1.51, 1.53	1.75-1.80	46
Sn(DMSO) ₂ (C ₆ H ₅) ₂ Cl ₂	2.28, 2.35		124.5, 133.7	1.52, 1.54	1.75, 1.77, 1.81	47
[Sn(C ₆ H ₅) ₂ NO ₃ (DMSO) ₃](NO ₃)	2.18		122.1, 136.3	1.47, 1.54, 1.55	1.75-1.80	48
Sn(DMSO) ₂ (CH ₃) ₂ Cl ₂	2.32, 2.38		117	1.51, 1.61	1.75-1.85	49
La(NO ₃) ₃ ·4DMSO	2.47, 2.48			1.48, 1.53	1.75-1.82	50
Nd(NO ₃) ₃ ·4DMSO	2.36, 2.38		137.0	1.50, 1.52	1.77, 1.78, 1.79, 1.96	51
Er(NO ₃) ₃ ·3DMSO	2.24, 2.27, 2.29		124.8, 131.1, 133.1	1.47, 1.62	1.68-2.00	52
Yb(NO ₃) ₂ ·3DMSO	2.23, 2.24, 2.26			1.29-1.51	1.71-1.84	53
Lu(NO ₃) ₃ ·3DMSO	2.15, 2.22, 2.40		126.8, 130.5, 135.0	1.32, 1.60, 1.70	1.51-2.07	54
[Hg(DMSO) ₆](ClO ₄) ₂	2.32, 2.38		117.3, 120.1, 132.2	1.51, 1.52	1.76-1.79	VII
Pb(NCS) ₂ ·2DMSO	2.45, 2.50		123.7, 128.2	1.50, 1.53	1.72-1.81	55
PbBr ₂ ·2DMSO	2.50		115.6	1.59	1.80	56
Th(DMSO) ₂ (8-Quinololito) ₄	2.36		1.38	1.52		57

Compound	M-S distance (Å)	M-O distance (Å)	M-O-S angle(deg.)	S-O distance (Å)	S-C distance (Å)	Ref
O-bonded:						
Fe(DMSO) ₂ Cl ₃		2.01	124.5	1.54	1.80	38
Cu(DMSO) ₂ Cl ₂		1.96	118.2	1.53	1.77	39
[Cu(DMSO)(C ₅ H ₅ NO)Cl ₂] ₂		2.28		1.55	1.82, 1.84	41
[Zn(DMSO) ₆](ClO ₄) ₂		2.10, 2.12	119.9	1.49	1.75-1.82	VI
[RuBr ₂ (NO)(DESO) ₂]Br		2.05	123.9	1.54	1.82, 1.83	42
[Cd(DMSO) ₆](ClO ₄) ₂		2.26	121-131	1.52-1.57	1.74-1.80	43
SnCl ₄ (DMSO) ₂				1.51, 1.54		44
Sn(CH ₃) ₂ Br ₂ (DMSO) ₂		2.27, 2.31	119.0, 125.2	1.56, 1.58	1.77-1.82	45
Sn(C ₆ H ₅) ₂ Cl ₂ (DMSO) ₂		2.28, 2.30	126.5, 142.0	1.51, 1.53	1.75-1.80	46
Sn(DMSO) ₂ (C ₆ H ₅) ₂ Cl ₂		2.28, 2.35	124.5, 133.7	1.52, 1.54	1.75, 1.77, 1.81	47
[Sn(C ₆ H ₅) ₂ NO ₃ (DMSO) ₃](NO ₃)		2.18	122.1, 136.3	1.47, 1.54, 1.55	1.75-1.80	48
Sn(DMSO) ₂ (CH ₃) ₂ Cl ₂		2.32, 2.38	117	1.51, 1.61	1.75-1.85	49
La(NO ₃) ₃ ·4DMSO		2.47, 2.48		1.48, 1.53	1.75-1.82	50
Nd(NO ₃) ₃ ·4DMSO		2.36, 2.38	137.0	1.50, 1.52	1.77, 1.78, 1.79, 1.96	51
Er(NO ₃) ₃ ·3DMSO		2.24, 2.27, 2.29	124.8, 131.1, 133.1	1.47, 1.62	1.68-2.00	52
Yb(NO ₃) ₂ ·3DMSO		2.23, 2.24, 2.26		1.29-1.51	1.71-1.84	53
Lu(NO ₃) ₃ ·3DMSO		2.15, 2.22, 2.40	126.8, 130.5, 135.0	1.32, 1.60, 1.70	1.51-2.07	54
[Hg(DMSO) ₆](ClO ₄) ₂		2.32, 2.38	117.3, 120.1, 132.2	1.51, 1.52	1.76-1.79	VII
Pb(NCS) ₂ ·2DMSO		2.45, 2.50	123.7, 128.2	1.50, 1.53	1.72-1.81	55
PbBr ₂ ·2DMSO		2.50	115.6	1.59	1.80	56
Th(DMSO) ₂ (8-Quinololito) ₄		2.36	1.38	1.52		57

Compound	M-S distance (Å)	M-O distance (Å)	M-O-S angle(deg.)	S-O distance (Å)	S-C distance (Å)	Ref
O-bonded:						
[UCl ₂ (DMSO) ₆][UCl ₆]		2.36	1.38	1.52		58
UO ₂ F ₂ (DMSO)		2.35	1.31	1.54	1.67	59
<u>a</u> Terminal DMSO	<u>b</u> S-bonded	<u>c</u> O-bonded				

A great practical advantage of DMSO is the convenient liquid range, 18.5 to 189°C.⁶¹ DMSO is also easily purified by distillation under reduced pressure.⁶² Other physical properties, compilations and dangers of DMSO has been given in a review by Reynolds.⁶¹

Ammonium perchlorate has been chosen as ionic medium, as not only the perchlorate, but also the ammonium halides and the ammonium thiocyanate are soluble to 1 M.

In the present investigation, the thermodynamics of the complexes formed by mercury(II) with chloride, bromide, iodide and thiocyanate systems have been studied in diluted solutions.^{II} Also the structures of the complexes have been determined in concentrated solutions.^{VIII, IX, 14, 15}

In order to study the influence of the ionic media, the thermodynamics of the complex formation has been measured at a lower concentration of ammonium perchlorate than earlier used, and also in other perchlorate media.^{III, IV} The complex formation of the zinc(II) bromide, cadmium(II) chloride, bromide, iodide and mercury(II) bromide systems have been studied potentiometrically and calorimetrically in 0.1 M ammonium perchlorate.^{III} The systems have been chosen so that the influence of a large medium change could be checked for both metal ions and ligands of vastly different bonding characteristics. Ammonium perchlorate is the only inert anhydrous supporting electrolyte which has been found not to oxidize zinc and cadmium amalgam or metallic mercury.^{IV} Potentiometric measurements could therefore not be performed in ionic media other than ammonium perchlorate. The complex formation in the media 0.1 M and 1 M lithium perchlorate, 1 M sodium perchlorate and 0.1 M tetraethylammonium perchlorate could only be studied calorimetrically.^{IV} The most suitable system for calculating both stability constants and enthalpy changes from calorimetric measurements is cadmium(II) bromide. In this system both the stability constants and the enthalpy changes are of suitable magnitude⁶³ both absolute, and relative to each other. In addition, zinc(II) bromide has been investigated in 1 M sodium perchlorate to check an earlier result very different from those found in 0.1 M and 1 M ammonium perchlorate.^{III, 10, 11}

As pointed out above a comparison between the thermochemical data and the structure of the complexes formed is of great interest. The initial species are the metal ions. The structure of the DMSO solvates of zinc(II), cadmium(II) and mercury(II) ions have been determined both in solution and in solid state by x-ray diffraction methods supplemented by raman and infrared spectroscopic measurements.^{V-VII, 43} The mercury(II) halide and thiocyanate systems are especially suitable for structural measurements in solution, because all complexes are dominating to at least 90 % in their range of existence except for the third mercury(II) thiocyanate complex.^{II, 64} Mercury is moreover a heavy atom, which scatters x-ray radiation very well. The structural investigations of the " HgX^+ " and HgX_4^{2-} complexes in DMSO solution are a continuation of the study of Johansson and Sandström of the structures of HgX_2 , HgX_3^- , HgBr_4^{2-} and HgI_4^{2-} complexes in DMSO solution.^{14, 15} They have also studied the structures HgX_3^- and HgX_4^{2-} , $\text{X} = \text{Cl}, \text{Br}$ and I , in aqueous solution.^{65, 66} The structural investigation on the mercury(II) thiocyanate system in DMSO solution includes the three complexes^{IV}, $\text{Hg}(\text{SCN})_n^{2-n}$, $n = 2-4$. The thermodynamics of this system differs markedly from the pattern found for the halides^{II}, and it is of interest to find out whether this is reflected in the structures of the complexes. The structural investigations of the zinc(II) and cadmium(II) thiocyanate systems were performed in order to establish the mode of coordination in these complexes. In aqueous solution zinc(II) coordinates the thiocyanate via nitrogen and mercury(II) via sulfur⁶⁷ as has been found by raman and infrared spectroscopic measurements. How thiocyanate is coordinated to cadmium(II) in aqueous solution⁶⁸ is so far not clear.

2. EXPERIMENTAL METHODS

2.1. Potentiometric measurements

The stability constants of the zinc(II) bromide and the cadmium(II) halide complexes in ammonium perchlorate medium have been determined potentiometrically by means of amalgam electrodes.⁶⁹ The procedure is described in detail previously.^{8, 10} The stability constants of the mercury(II) halide and thiocyanate systems have

been determined potentiometrically by means of a mercury pool electrode.^{II} In this case, the potentiometric titrations must start at high ligand numbers, because mercury(II) has to be stabilized by ligands forming strong complexes in order not to react with metallic mercury to mercury(I).^I A mercury(II) solution containing a large excess of ligand or a pure ligand solution was therefore titrated with a mercury(II) solution. The mercury(II) solutions were freshly prepared each day, as the mercury(II) contents in DMSO solutions decreases with time.^{II} The titration series were interrupted at a ratio $\frac{C_L}{C_M} \approx 1.5$, as the reproporationation reaction becomes perceptible below this ratio. The reproporationation constant, $K_R = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$ in DMSO is 24.5 and 37 in 1M and 0.1M ammonium perchlorate, respectively.^I For all systems measured the reproducibility of the emfs was very good at all ligand concentrations.

2.2. Calorimetric measurements

The calorimetric measurements were performed in a titration calorimeter described elsewhere.^{70, 71} The heats of dilution for the metal and the ligand ions have been performed as described previously.^{72, 73} Also for the mercury(II) complexes HgX^+ , HgX_2 and HgX_3^- , $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and SCN , the heats of dilution have been measured. This is possible as all these complexes except the $\text{Hg}(\text{SCN})_3^-$ complex, at their maxima contribute >90 % of the total mercury(II) content. The mercury(II) thiocyanate measurements could not be performed in a gold reaction vessel on account of the strong complex formation of gold(I) with thiocyanate both absolute and relative to mercury(II). Metallic gold is oxidized, with the formation of metallic mercury. The reaction takes place very rapidly, the gold vessel being at once covered with amalgam. The thiocyanate system has therefore been investigated in a rhodium plated gold vessel. The details of the procedure used and of the titration series are described elsewhere.^{II}

2.3. Raman and infrared measurements

The Raman spectra were recorded on a Cary 82 argon ion laser Raman spectrophotometer, using the 4880 Å line. Glass tubes of 1 mm

diameter were used as sample holders both for the solids and the solutions. The infrared spectra were recorded on a Perkin-Elmer 221 or Beckman IR-9 infrared spectrophotometer. In the low-frequency range, $400\text{--}150\text{ cm}^{-1}$, the measurements were performed on a RII C F5-720 Fourier spectrometer at liquid nitrogen temperature. This low-frequency infrared measurements were performed at the Department of Inorganic Chemistry, University of Uppsala. Depending upon substance and frequency, various techniques have been used: polyethene and KRS-5 windows, Nujol mulls and KBr pellets.

2.4. X-Ray diffraction measurements on solids

$[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2(\text{S})$. The determination of space group and preliminary values of the unit cell has been performed on a Weissenberg camera. The intensity data for the determination of the crystal molecular structure have been collected by a CAD 4 diffractometer with a low temperature equipment, at 246 K.

$[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2(\text{S})$. The intensity data were collected by a Syntex P2₁ computer-controlled four-circle diffractometer, equipped with a scintillation counter. This work has been performed at the Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm.

2.5. X-Ray diffraction measurements on solutions

The $\theta\text{--}\theta$ diffractometers used for the measurements of the X-ray scattering apply the Bragg-Brentans para-focusing geometry. The scattering angle 2θ is changed by moving the X-ray tube and the detector arrangement symmetrically in opposite directions around the horizontal axis through the sample, Fig. 1. The container with the solution is enclosed in an air-tight radiation shield with beryllium windows for the X-rays. MoK_α radiation and LiF monochromator were used in all measurements. The intensity of the diffracted X-ray beam was measured by a scintillation counter. The amount of incoherent scattering reaching the scintillation counter was estimated in a semi-empirical way.^V The scattered intensity was repeated twice at discrete points in the range

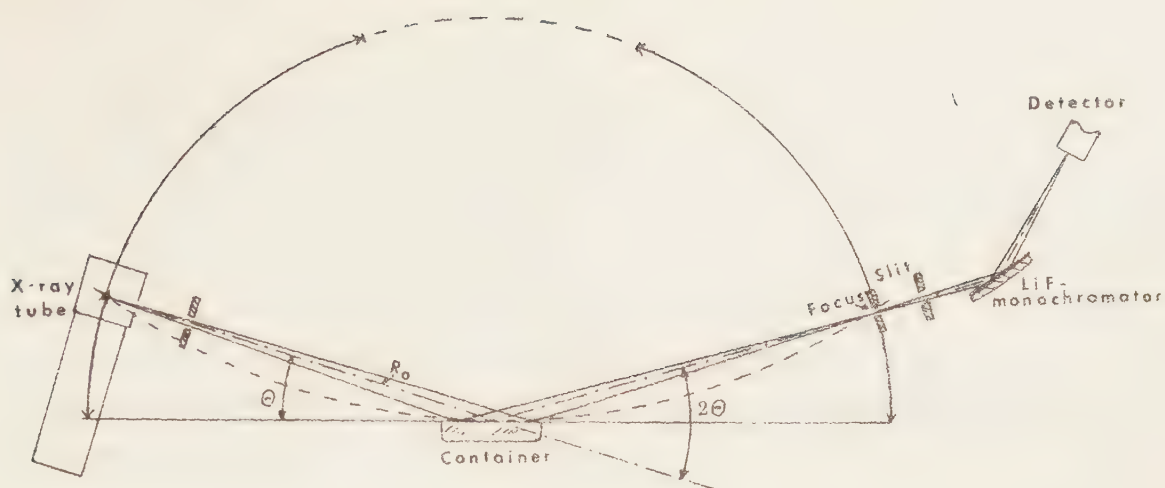


Fig. 1. The principle of the θ - θ diffractometer used for the X-ray diffraction measurements. The focal slit and the X-ray source move in opposite directions stepwise along a circular arc for $1^\circ < \theta < 63^\circ$. (From Sandström, Diss. 1978, Royal Institute of Technology).

$1.00^\circ \leq \theta \leq 62.55^\circ$, where 2θ is the scattering angle, at intervals of 0.10° for the range $1.00^\circ \leq \theta \leq 30.00^\circ$, and of 0.25° for the range $19.80^\circ \leq \theta \leq 62.55^\circ$. All measurements were performed at $25 \pm 1^\circ\text{C}$. The data treatment is excellently described by Sandström et.al.⁶⁶ This large-angle scattering measurements have been performed at the Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, and at the Department of Inorganic Chemistry, University of Gothenburg, Gothenburg.

3. CALCULATIONS

3.1. Calculations in the thermodynamic measurements

From the emfs measured of the zinc(II) and cadmium(II) systems, the stability constants have been calculated by the computer program "EMK".⁷⁴ After some modifications of the program "EMK",^{II} it could also be used for the reversed potentiometric used for the mercury(II) halide and thiocyanate systems.

From the calorimetric measurements the enthalpy changes have been calculated by the computer program "KALORI".⁷⁴ Both enthalpy changes and stability constants could in principle be calculated by this program. In practice, this is possible for the zinc(II) and cadmium(II) but not for the mercury(II) systems. For those

the stability constants determined potentiometrically have been used as fixed parameters. In the final calculations of the enthalpy changes of the zinc(II) and cadmium(II) halide systems in ammonium perchlorate weighted mean values of the stability constants from the potentiometric and calorimetric measurements have been used as fixed parameters. An extensive discussion of calculations of equilibrium constants from calorimetric data is given elsewhere.⁶³

3.2. Calculations for structure determinations of solids

Existing computer programs for calculations of cell dimensions and molecular structures have been used. These are listed elsewhere.^{75, 76}

3.3. Calculations for structure determinations in solution

All calculations were performed by means of the KURVLR and PUTSLR computer programs.⁷⁷ The raw data of each measured point is the time needed for a scintillation counter to register a certain number of counts, normally 40.000 to 100.000. The intensity in a point is given by the ratio number of counts/time in seconds, corresponding to 1° slit system. The reduced intensity curves, $i(s)$, were calculated for each experimental point from

$$i_{\text{obs}}(s) = I_{\text{obs}}(s) - \sum_m \left\{ \left(\frac{f_m(s) + \Delta f'_m}{\underline{m}} \right)^2 + \left(\frac{\Delta f''_m}{\underline{m}} \right)^2 + \right. \\ \left. + \frac{\text{del}(s) (\lambda/\lambda')^3}{\underline{m}} \sum_m I_{\text{incoh}}(s) \right\}$$

where s is the angle dependence, $s = 4\pi\lambda^{-1}\sin\theta$ and $I_{\text{obs}}(s)$ is the corrected and normalized intensity. The summations are performed over all atoms m in a stoichiometric unit of the volume, V . RHF scattering factors, f , for the ions and the neutral atoms were used,⁷⁸ except for H, where the spherical form factors proposed by Stewart et.al.⁷⁹ were employed. Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were applied for all atoms.⁸⁰ The incoherent scattering factors, I_{incoh} , were taken from Cromer and Mann⁸¹, Cromer⁸² and Compton and Allison⁸³. Correction for the Breit-Dirac factor^{84, 85} in a form appropriate to a

scintillation counter⁸⁶, $(\lambda/\lambda')^3$, was applied. The function $\text{del}(\underline{s})$, describes the fraction of the incoherent radiation which passes the monochromator. The electronic radial distribution functions, $\underline{D}(\underline{r})$, were calculated as

$$\underline{D}(\underline{r}) = 4\pi \underline{r}^2 \rho_0 + (2\underline{r}/\pi) \int_{\underline{s}_{\min}}^{\underline{s}_{\max}} \underline{s}(\underline{s}) \underline{\text{Mod}}(\underline{s}) \sin(\underline{r}\underline{s}) d\underline{s}$$

where the modification function $\underline{\text{Mod}}(\underline{s})$, was $\{f_{\underline{m}}^2(0)/f_{\underline{m}}^2(\underline{s})\} \times \exp(-0.010\underline{s}^2)$, ($\underline{M} = \text{Zn, Cd or Hg}$) and $\rho_0 = \{(\sum(f_{\underline{m}} + \Delta f_{\underline{m}}'))^2 + (\sum \Delta f_{\underline{m}}'')^2\}/V$. A correction was made for errors giving low-frequency additions to the $i(\underline{s})$ curves. Small spurious peaks below 1.5-1.7 Å in the function $(\underline{D}(\underline{r}) - 4\pi \underline{r}^2 \rho_0 - \sum f_{\underline{j}} \text{calc})$, which could not be related to interatomic distances in DMSO and in the perchlorate ion, which are well-known, were removed by a Fourier transformation procedure.⁸⁷

In the least-squares refinements, the parameter values of the models used for calculations of intramolecular intensity contributions were refined, using the high angle regions of the intensity curves. Series of refinements were performed, where a minimum was sought for the weighted error-square-sum

$$\sum_{\underline{s}_{\min}}^{\underline{s}_{\max}} \underline{w}(\underline{s}) \{i_{\text{obs}}(\underline{s}) - i_{\text{calc}}(\underline{s})\}^2. \text{ The weighting function, } \underline{w}(\underline{s}), \text{ was}$$

proportional to $\underline{I}_{\text{obs}}^{-1} \cos \theta$, which gives each part of the refined $i(\underline{s})$ curve a weight corresponding approximately to its statistical precision and also compensates for the unequal spacing between the points caused by the constant $\Delta\theta$ intervals used during the intensity measurements. To check for correlations between the parameters of the tested models, different combinations of parameters were refined. The influence of systematic errors in different parts of the intensity curves were estimated by using different $\underline{s}$ ranges in the refinements. Especially the lower limit of the $\underline{s}$ range was varied. Parameters which were known previously, such as bond distances, bond angles and temperature factor coefficients of the DMSO molecule and the perchlorate ion, the number of bonds in HgX_4^{2-} , etc., were introduced as fixed parameters.

4. RESULTS

4.1. Standard Electrode Potentials in dimethylsulfoxide solution

The standard electrode potentials of the metal redox systems of groups IB and IIB in water and DMSO, with the $\text{Ag(s)}/\text{Ag}^+$ electrode in water as reference electrode, are given in Fig. 2. The potentials are taken from Ahrlund et.al.^{1, 10, 88, 89} and from Handbook of Chemistry and Physics⁹⁰. The difference between the $\text{Ag(s)}/\text{Ag}^+$ electrodes in aqueous and DMSO solution is calculated from the free energy of transfer, $\Delta G_{\text{tr}}^{\circ}$, according to the formula $\Delta G_{\text{tr}}^{\circ} = -nF \cdot \Delta E$. The value⁹¹ of $\Delta G_{\text{tr}}^{\circ} = -33.7 \text{ kJmol}^{-1}$ gives that it corresponds to a value of E° in DMSO 349 mV more negative than in water. All metals investigated are less noble in DMSO than in water, Fig. 2. This depends on that the metal ions have higher solvation enthalpies in DMSO than in water.

As seen in Fig. 2, d^{10} ions are more favoured in DMSO than in water. This behaviour is more marked for a transfer of these metal ions from water to pyridine.⁹² Pyridine solvates metal ions through its very soft nitrogen atom and stabilizes d^{10} ions markedly^{92, 93}.

4.2. Solvent exchange reactions between dimethylsulfoxide and water

The thermodynamics of solvent exchange reactions between DMSO and water for the zinc(II), cadmium(II), mercury(II) and silver(I) ions are given in Table 2. The exchange free energy,

Table 2. Equilibrium constants, K_{ex} , and thermodynamic functions ($\Delta G_{\text{ex}}^{\circ}$, $\Delta H_{\text{ex}}^{\circ}/\text{kJmol}^{-1}$; $\Delta S_{\text{ex}}^{\circ}/\text{JK}^{-1}\text{mol}^{-1}$) for the reactions $\text{M}^{n+}(\text{DMSO}, \underline{I}=1) + n \text{Ag}^+(\text{aq}) \rightleftharpoons \text{Mn}^+(\text{aq}) + n \text{Ag}^+(\text{DMSO}, \underline{I}=1)$, at 25°C

M^{n+}	K_{ex}	$-\Delta G_{\text{ex}}^{\circ}$	$-\Delta H_{\text{ex}}^{\circ}$	$\Delta S_{\text{ex}}^{\circ}$
Cu^+	0.096	-5.8		
Cu^{2+}	2130	19.0		
Zn^{2+}	3750	20.4	50	-99
Cd^{2+}	99	11.4	43	-106
Hg^{2+}	0.75	-0.7	34	-116
Hg_2^{2+}	2.3	2.1		

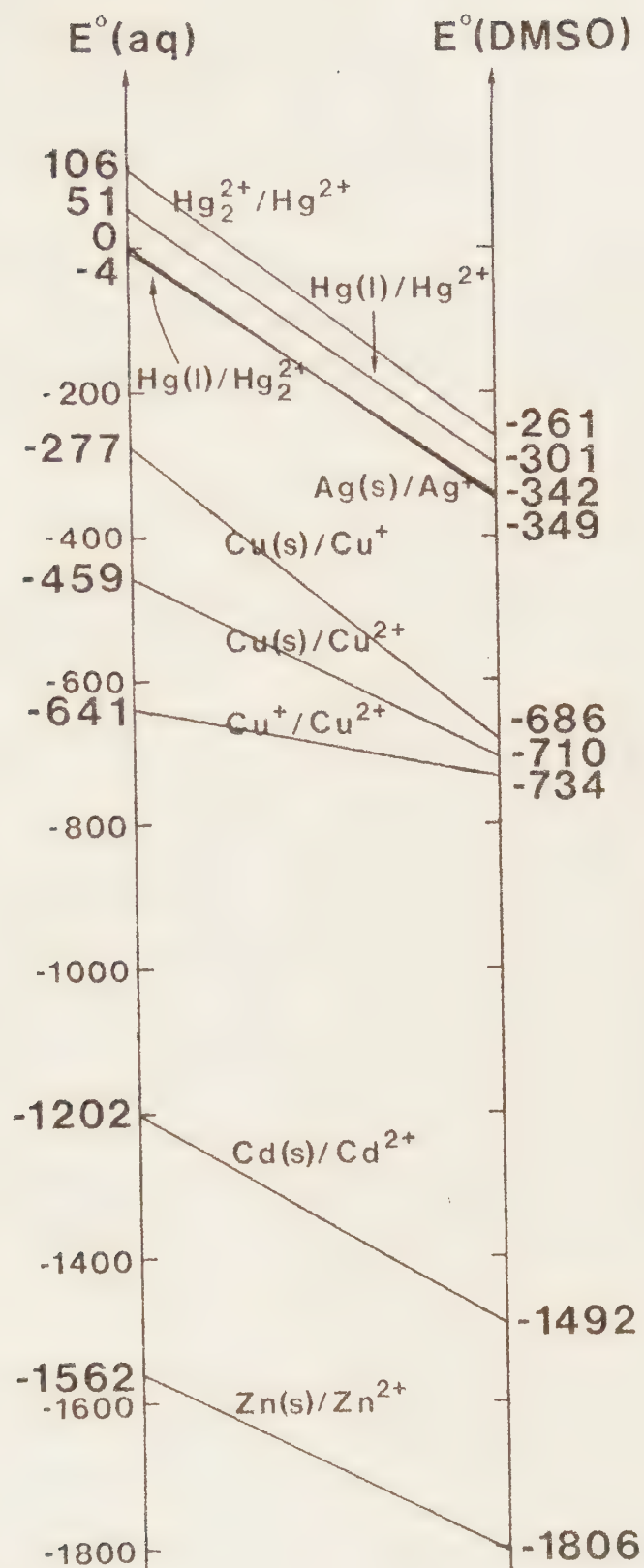


Fig. 2. Standard electrode potentials in aqueous and dimethylsulfoxide solution, referred to $E^\circ(\text{aq}) = 0$ for the $\text{Ag(s)}/\text{Ag}^+$ electrode.

$\Delta G_{\text{ex}}^{\circ}$, for these reactions are calculated from the difference of the standard electrode potential in water and DMSO, according to¹⁰
 $\Delta G_{\text{ex}}^{\circ} = -nF\Delta E^{\circ}$. The enthalpy changes, $\Delta H_{\text{ex}}^{\circ}$, for these reactions are given elsewhere.^{16, 84} The entropy changes, $\Delta S_{\text{ex}}^{\circ}$, are calculated by the formula $\Delta S_{\text{ex}}^{\circ} = (\Delta H_{\text{ex}}^{\circ} - \Delta G_{\text{ex}}^{\circ})/T$.

All solvent exchange reactions involving transfer of silver(I) from water to DMSO are strongly entropy destabilized, Table 2. Silver evidently brings about a marked increase of order when moved from water to DMSO.

4.3. Stability constants and thermodynamic functions

4.3.1. The mercury(II) halide and thiocyanate systems in 1 M ammonium perchlorate

Equilibrium constants, K_j , and thermodynamic functions ΔG_j° , ΔH_j° and ΔS_j° for the stepwise formation of mercury(II) chloride, bromide, iodide and thiocyanate complexes in DMSO and water are given in Table 3. The free energy changes, ΔG_j° , are calculated from the stepwise stability constants, K_j , according to the formula $\Delta G_j^{\circ} = -RT \ln K_j$. Combined with the calorimetrically determined enthalpy changes, ΔH_j° , they yield the entropy changes, ΔS_j° . Both potentiometric and calorimetric measurements indicate four mononuclear complexes in diluted solution.^{II} The mononuclear complexes HgX_2 , HgX_3^- and HgX_4^{2-} exist over a very wide concentration range of C_M , as has been confirmed by structural and spectroscopic investigations.¹⁵ The complex HgX^+ , on the other hand, disproportionates as C_M increases.^{VIII, IX}

4.3.2. The zinc(II) bromide, cadmium(II) chloride, bromide and iodide and mercury(II) bromide systems in 0.1 M ammonium perchlorate

The stepwise stability constants, K_j , the ratios K_j/K_{j+1} , and the thermodynamic functions, for 0.1 M and 1 M ammonium perchlorate media, are given in Tables 4 och 5. Both the potentiometric and the calorimetric measurements indicate three

Table 3. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJ\text{mol}^{-1}$; $\Delta S_j^\circ/JK^{-1}\text{mol}^{-1}$) for the stepwise formation of mercury(II) halide and thiocyanate complexes in DMSO and water, at 25°C

DMSO					Water			
NH_4ClO_4 , 1.0 M					NaClO_4 , 0.5 M		1.0 M	
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-
$\log K_1$	10.87	12.14	13.52	9.33	6.74	9.05	12.87	9.08
$\log K_2$	7.10	8.06	9.76	5.66	6.48	8.28	10.95	7.78
$\log K_3$	3.99	5.14	6.01	2.96	0.85	2.41	3.78	2.84
$\log K_4$	2.08	2.54	2.62	2.31	1.00	1.26	2.23	1.97
K_1/K_2	5.9×10^3	1.2×10^4	5.8×10^3	4.7×10^3	1.8	5.9	83	20
K_2/K_3	1.3×10^3	830	5.5×10^3	510	4×10^5	7×10^5	1.5×10^7	9×10^4
K_3/K_4	82	400	2.5×10^3	4.4	0.7	14	35	7
$-\Delta G_1^\circ$	62.0	69.3	77.2	55.3	38.5	51.7	73.5	51.8
$-\Delta G_2^\circ$	40.5	46.0	55.7	32.2	37.0	47.3	62.5	44.4
$-\Delta G_3^\circ$	22.8	29.3	34.3	16.9	4.9	13.8	21.6	16.2
$-\Delta G_4^\circ$	11.9	14.5	15.0	13.2	5.7	7.2	12.7	11.2
$-\Delta H_1^\circ$	20.3	24.7	33.2	28.1	24.7	42.2	75.3	49.7
$-\Delta H_2^\circ$	28.5	31.9	39.4	31.1	28.9	44.8	67.8	50.4
$-\Delta H_3^\circ$	20.1	27.8	28.1	9.7	9.2	12.0		20.4
$-\Delta H_4^\circ$	14.0	19.1	21.1	16.8	0.4	17.2		21.0
ΔS_1°	140	149	148	85	46	32	-6	7
ΔS_2°	40	47	54	4	27	8	-18	-20
ΔS_3°	9	5	21	24	-14	6		-14
ΔS_4°	-7	-16	-21	-12	20	-33		-33
$-\Delta H_{\beta 4}^\circ$	82.9	103.5	121.8	85.6	62.4	116.2	185	141.5
$\Delta S_{\beta 4}^\circ$	182	186	202	100	79	13	-49	-60
Ref	II				94-96	94, 97	94, 98	99

Table 4. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJ\text{mol}^{-1}$; $\Delta S_j^\circ/JK^{-1}\text{mol}^{-1}$) for the stepwise formation of cadmium(II) chloride, biomide and iodide complexes in DMSO at 25°C

	0.1 M NH_4ClO_4			1 M NH_4ClO_4		
	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
$\log K_1$	4.36	3.69	2.57	3.23	2.92	2.18
$\log K_2$	2.92	2.50	1.80	1.97	1.91	1.37
$\log K_3$	3.46	3.28	2.83	2.58	2.75	2.93
$\log K_4$	2.34	1.83	1.13	1.75	1.68	1.18
K_1/K_2	27	16	5.9	18	10	6.4
K_2/K_3	0.29	0.17	0.09	0.24	0.15	0.03
K_3/K_4	13	28	58	6.7	12	58
$-\Delta G_1^\circ$	24.9	21.0	14.7	18.4	16.7	12.5
$-\Delta G_2^\circ$	16.7	14.2	10.3	11.2	10.9	7.8
$-\Delta G_3^\circ$	19.7	18.7	16.2	14.7	15.7	16.8
$-\Delta G_4^\circ$	13.4	10.4	6.1	10.0	9.5	6.7
$-\Delta H_1^\circ$	4.9	0.9	-5.2	6.3	3.9	-2.4
$-\Delta H_2^\circ$	-12.5	-15.8	-21.5	-15	-17	-27
$-\Delta H_3^\circ$	-6.7	-7.2	-6.6	-1	-2	5
$-\Delta H_4^\circ$	15.5	11.4	4.8	12.2	13	9.5
ΔS_1°	67	68	67	41	43	50
ΔS_2°	98	101	106	88	94	117
ΔS_3°	88	87	76	53	59	40
ΔS_4°	-7	-3	4	-7	-12	-10
$-\Delta H_4^\circ$	1.2	-10.7	-38.1	2	-2.1	-15
$\Delta S_{\beta 4}^\circ$	246	253	253	175	184	197
Ref	III			8,9		

Table 5. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJ\text{mol}^{-1}$; $\Delta S_j^\circ/JK^{-1}\text{mol}^{-1}$) for the stepwise formation of zinc(II), cadmium(II) and mercury(II) bromide complexes in DMSO at 25°C.

	0.1 M NH_4ClO_4			1 M NH_4ClO_4		
	Zn^{2+}	Cd^{2+}	Hg^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}
$\log K_1$	1.86	3.69	12.92	0.85	2.92	12.14
$\log K_2$	3.31	2.50	9.05	2.89	1.91	8.06
$\log K_3$	1.98	3.28	5.66	1.35	2.75	5.14
$\log K_4$		1.83	2.60		1.68	2.54
K_1/K_2	0.04	16	7.5×10^3	0.09	10	1.2×10^4
K_2/K_3	21	0.17	2.4×10^3	35	0.15	8.3×10^2
K_3/K_4		28	1.2×10^3		12	4.0×10^2
$-\Delta G_1^\circ$	10.6	21.0	73.7	4.8	16.7	69.3
$-\Delta G_2^\circ$	18.9	14.2	51.6	16.5	10.9	46.0
$-\Delta G_3^\circ$	11.3	18.7	32.3	7.7	15.7	29.3
$-\Delta G_4^\circ$		10.4	14.8		9.5	14.5
$-\Delta H_1^\circ$	-22.3	0.9	20.0	-27.8	3.9	24.7
$-\Delta H_2^\circ$	-19.9	-15.8	24.1	-9.1	-17	31.9
$-\Delta H_3^\circ$	5.9	-7.2	24.4	4.2	-2	27.8
$-\Delta H_4^\circ$		11.4	17.3		13	19.1
ΔS_1°	110	68	180	110	43	149
ΔS_2°	130	101	92	85	94	47
ΔS_3°	18	87	26	12	54	5
ΔS_4°		-3	-8		-12	-16
$-\Delta H_3^\circ$	-36.3	-22.1	68.5	-32.7	-15	84.4
ΔS_3°	258	256	298	207	196	201
Ref	III			10, 11	8, 9	II

Table 6. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions ($\underline{\Delta G}_j^0$, $\underline{\Delta H}_j^0/kJ\text{mol}^{-1}$; $\underline{\Delta S}_j^0/JK\text{mol}^{-1}$) for the stepwise formation of cadmium(II) bromide systems in different ionic media in DMSO at 25°C

	1.00 M NH_4ClO_4	0.10 M NH_4ClO_4	1.00 M NaClO_4	1.00 M LiClO_4	0.10 M LiClO_4	0.10 M Et_4NClO_4
$\log K_1$	2.92	3.69	3.48	3.56	3.79	3.92
$\log K_2$	1.91	2.50	2.36	2.93	3.07	2.88
$\log K_3$	2.75	3.28	3.17	2.94	3.05	3.40
$\log K_4$	1.68	1.83	1.86	3.35	3.11	2.21
K_1/K_2	10	16	13	4.3	5.3	11
K_2/K_3	0.15	0.17	0.15	0.96	1.1	0.30
K_3/K_4	12	28	21	0.39	0.88	16
$-\underline{\Delta G}_1^0$	16.7	21.0	19.9	20.3	21.6	22.4
$-\underline{\Delta G}_2^0$	10.9	14.2	13.5	16.7	17.5	16.5
$-\underline{\Delta G}_3^0$	15.7	18.7	18.1	16.8	17.4	19.4
$-\underline{\Delta G}_4^0$	9.5	10.4	10.6	19.1	17.7	12.6
$-\underline{\Delta H}_1^0$	3.9	0.9	2.8	0.3	-0.3	0.0
$-\underline{\Delta H}_2^0$	-17	-15.8	-13.6	-3.1	-0.4	-17.9
$-\underline{\Delta H}_3^0$	-2	-7.2	-6.6	-23.9	-27.5	-7.3
$-\underline{\Delta H}_4^0$	13	11.4	13.4	10.5	10.9	9.5
$\underline{\Delta S}_1^0$	43	68	57	67	73	75
$\underline{\Delta S}_2^0$	94	101	91	66	72	115
$\underline{\Delta S}_3^0$	59	87	83	137	151	90
$\underline{\Delta S}_4^0$	-12	-3	-9	29	23	10
$-\underline{\Delta H}_4^0$	-2	-10.7	-4.0	-16.2	-20.8	-157
$\underline{\Delta S}_{\beta 4}^0$	184	252	221	299	319	290
Ref	8, 9	III	IV			

mononuclear complexes for the zinc(II) bromide system, while the cadmium(II) halides and mercury(II) bromide form four mononuclear complexes.

4.3.3. The zinc(II) and cadmium(II) bromide systems in various perchlorate media

In addition to the measurements in ammonium perchlorate media, zinc(II) and cadmium(II) have been studied in 1 M sodium perchlorate, and the latter system also in 0.1 M and 1 M lithium and 0.1 M tetraethylammonium perchlorate. These media all attack zinc and cadmium amalgam and metallic mercury, and cannot therefore be used for potentiometric measurements. Consequently, both stability constants and enthalpy changes are determined calorimetrically. The stepwise stability constants, K_j , the ratios K_j/K_{j+1} , and the thermodynamic functions are in Table 6.

4.4. The structure of crystalline zinc(II) and mercury(II) DMSO solvates

The crystal and molecular structures of $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ and $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$ have been determined by X-ray diffraction methods.^{VI, VII} Both structures persist of hexakis(dimethylsulfoxide)metal cations of perchlorate anions. The metal ions coordinate six DMSO molecules through the oxygen atoms, forming almost regular octahedrons. Also the sulfur atoms are arranged almost octahedrally around the central atoms. The S-O distances in coordinated DMSO molecules are slightly longer and the S-C distances are slightly shorter than in free DMSO. The important interatomic distances and bond angles in $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ and $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$ are given in Table 7. The structure of the coordination polyhedrons $\text{Zn}(\text{DMSO})_6^{2+}$ and $\text{Hg}(\text{DMSO})_6^{2+}$ are shown in Figs. 3 and 4. The refined atomic parameters are given in the original papers.^{VI, VII}

Table 7. Intramolecular atomic distances (Å) and angles (degrees) in the compounds $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2(\text{s})$ and $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2(\text{s})$

Zn-O1	2.121(13)	Zn-O1-S1	117.8(7)
Zn-O2	2.098(13)	Zn-O2-S2	122.0(8)
Zn-S1	3.115(4)		
Zn-S2	3.154(5)		
Hg-O1	2.376(6)	Hg-O1-S1	120.1(3)
Hg-O2	2.320(6)	Hg-O2-S2	132.2(4)
Hg-O3	2.317(6)	Hg-O3-S3	117.3(4)
Hg-S1	3.404(2)		
Hg-S2	3.502(2)		
Hg-S3	3.302(2)		



Fig. 3. A stereoscopic view of the $\text{Zn}(\text{DMSO})_6^{2+}$ cation. All atoms are represented by 50 % probability thermal ellipsoids.

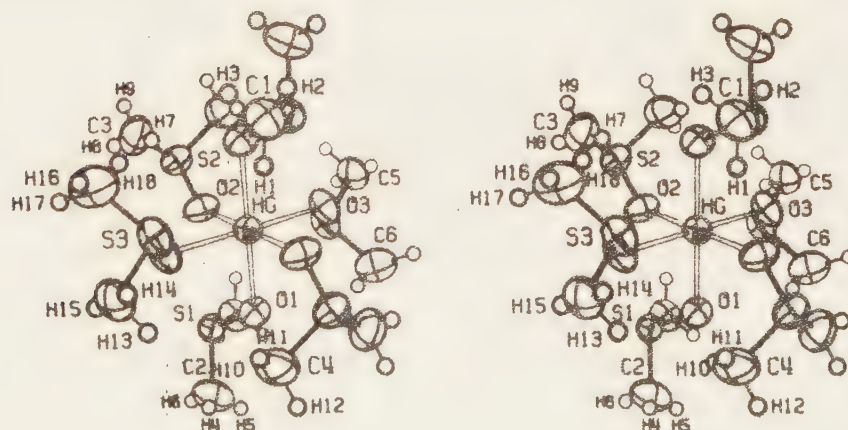


Fig. 4. A stereoscopic view of the $\text{Hg}(\text{DMSO})_6^{2+}$ cation. All non-H atoms are represented by 50 % probability thermal ellipsoids. For clarity the H atoms have been given a B-value of 1 Å^2 in the figure.

4.5. The structure of complexes formed in dimethylsulfoxide solution

4.5.1. The zinc(II), cadmium(II) and mercury(II) DMSO solvates

Saturated DMSO solutions of zinc(II), cadmium(II) and mercury(II) perchlorate have been investigated by raman spectroscopy and x-ray diffraction. The spectra shown that these metal ions coordinate DMSO via the oxygen atom.^V The radial distribution functions obtained from the x-ray diffraction measurements show relatively sharp peaks at 3.2, 3.4 and 3.4 Å and small smoothed peak or shoulders at 2.1, 2.3 and 2.4 Å for the zinc(II), cadmium(II) and mercury(II) solutions, respectively. These peaks correspond to metal-sulfur and metal-oxygen distances, respectively. The refinements gave more precise values of these distances which are given in Table 8, together with the temperature factor coefficients and the number of distances. The latter number is always close to six. Also in solution Zn^{2+} , Cd^{2+} and Hg^{2+} thus coordinate six DMSO via oxygen in a regular octahedral arrangements^{V, VI}, i.e. the structures are same as found in the solids^{VI, VII, 43} $[\text{M}(\text{DMSO})_6](\text{ClO}_4)_2$, $\text{M} = \text{Zn}, \text{Cd}$ and Hg .

Table 8. The refined parameters $\underline{d}$ =distance (Å), $\underline{b}$ =temperature factor coefficient ($\text{\AA}^2$) and $\underline{n}$ =number of distances per metal atom for the zinc(II), cadmium(II) and mercury(II) perchlorate DMSO solutions investigated by X-ray diffraction measurements

Interaction	Parameter	0.70M $\text{Zn}(\text{ClO}_4)_2$	0.69M $\text{Cd}(\text{ClO}_4)_2$	0.93M $\text{Hg}(\text{ClO}_4)_2$
M-O	$\underline{d}$	2.127(5)	2.290(3)	2.394(3)
	$\underline{b}$	0.0148(9)	0.0041(5)	0.010(1)
M-S	$\underline{d}$	3.147(3)	3.417(3)	3.426(3)
	$\underline{b}$	0.0158(6)	0.016(1)	0.018(1)
M-O and M-S	$\underline{n}$	6.0(1)	6.5(1)	5.6(2)

4.5.2. The mercury(II) chloride, bromide and iodide complexes

Extensive investigations of the structures of the mercury(II) halide complexes in DMSO have been performed previously.^{14, 15} However, the fourth mercury(II) chloride complex has not been studied and the first mercury(II) halide complexes gave partly unexpected results. For the mercury(II) chloride and bromide systems, the results were interpreted as indicating a partial disproportionation of HgX^+ into solvated Hg^{2+} and HgX_2 . The complex HgI^+ was assumed to disproportionate partly into Hg_2I^{3+} and HgI_2 . Further raman spectroscopic and x-ray diffraction measurements on solutions containing equal concentrations of mercury(II) and halide have now been performed in a much wider concentration range.^{VIII} Spectra of chloride and bromide solutions of $\underline{C}_L/\underline{C}_M = 1$ show $\nu_1(\text{Hg-X})$ frequencies corresponding to HgX_2 and a Hg-O bend frequency corresponding to $\text{Hg}(\text{DMSO})_6^{2+}$.^{13, VIII} This indicates that both $\text{Hg}(\text{DMSO})_6^{2+}$ and HgX_2 exist in these solutions, and that a disproportionation has occurred. The intensity of $\nu_1(\text{Hg-X})$ is approximate proportional to $\underline{C}_M$ in the range 0.30 M to saturated solution. For the chloride system, the disproportionation is found to be complete in 0.5 M solution, while in saturated solutions the disproportionation is again only partial.^{VIII, 15} For iodide solutions of $\underline{C}_L/\underline{C}_M = 1$ a $\nu_1(\text{Hg-I})$ frequency corresponding to the HgI_2 complex is found but no peak that can be related to $\text{Hg}(\text{DMSO})_6^{2+}$. On the other hand a new peak emerges at 173 cm^{-1} . This peak has been assigned to a Hg-I stretch frequency in the dinuclear ion Hg_2I^{3+} .¹⁰⁰ For mercury(II) concentrations $>0.25 \text{ M}$, the intensities of these peaks are proportional to the concentration. The HgI^+ complex would thus disproportionate completely into Hg_2I^{3+} and HgI_2 in concentrated solutions.

This has been confirmed by x-ray studies of solutions of $\underline{C}_M = 0.80 \text{ M}$ and $\underline{C}_L/\underline{C}_M = 1$. For chloride and bromide, the refinements gave the same results as earlier found for HgX_2 if half of the mercury(II) concentration was assumed to be present^{VIII} as $\text{Hg}(\text{DMSO})_6^{2+}$. For the iodide solution, the distance Hg-I, which is an average value of the distances in Hg_2I^{3+} and HgI_2 , was found

to be about the same as in HgI_2 .^{VIII} The terminal mercury atoms in Hg_2I^{3+} are certainly solvated, presumably by three DMSO per atom, completing tetrahedra.^{VIII} These DMSO molecules are at about the same distances to mercury as in the solvate $\text{Hg}(\text{DMSO})_6^{2+}$.

The x-ray structure determinations of HgCl_4^{2-} and HgBr_4^{2-} in DMSO showed that each mercury(II) ion was surrounded by four chloride and bromide ions, respectively, in regular tetrahedral configurations. The Hg-Cl and Hg-Br distances were found to be 2.532(2) and 2.628(2) Å, respectively. In the case of HgBr_4^{2-} the distance is in excellent agreement with that found earlier¹⁵ but they are slightly longer than found in aqueous solution^{65, 66} and in solid state¹⁰¹⁻¹⁰³. The HgX_2 , HgX_3^- and HgX_4^{2-} , X = Cl, Br, I and SCN, distances found in DMSO and in the solid state are given in Table 9, as are also the $\nu_1(\text{Hg-X})$ frequencies.

Table 9. Hg-X distances (Å) in solid state and DMSO solution and $\nu_1(\text{Hg-X})$ frequencies (cm^{-1}) in DMSO solution for the HgX_n^{2-n} complexes, n = 2-4 and X = Cl, Br, I and SCN. Standard deviations are given in parentheses.

	HgX_2	HgX_3^-	HgX_4^{2-}
	$\underline{d}(\text{solid})$	$\underline{d}(\text{solid})$	$\underline{d}(\text{solid})$
	2.280(7) ¹⁰⁴	2.432(3) ¹⁰⁵	2.495(10) ¹⁰¹ , 2.464(1) ¹⁰²
Cl	$\underline{d}(\text{solution})$	$\underline{d}(\text{solution})$	$\underline{d}(\text{solution})$
	2.350(3)*	2.434(3)*	2.532(2) ^{VIII}
	$\nu_1(\text{Hg-X})$	$\nu_1(\text{Hg-X})$	$\nu_1(\text{Hg-X})$
	303*	279*	260*
	$\underline{d}(\text{solid})$	$\underline{d}(\text{solid})$	$\underline{d}(\text{solid})$
	2.424(5) ¹⁰⁶	2.48(3)-2.56(3) ¹⁰⁷	2.588(4) ¹⁰³
Br	$\underline{d}(\text{solution})$	$\underline{d}(\text{solution})$	$\underline{d}(\text{solution})$
	2.455(2)*	2.547(3)*	2.628(2)*, VIII
	$\nu_1(\text{Hg-X})$	$\nu_1(\text{Hg-X})$	$\nu_1(\text{Hg-X})$
	194*	178*	164*
	$\underline{d}(\text{solid})$	$\underline{d}(\text{solid})$	$\underline{d}(\text{solid})$
	2.618(6) ¹⁰⁸	2.72(1) ¹⁰⁹	2.77(1) ¹¹⁰ , 2.783(3) ¹⁰⁸
I	$\underline{d}(\text{solution})$	$\underline{d}(\text{solution})$	$\underline{d}(\text{solution})$
	2.624(2)*	2.733(3) ¹⁴	2.796(3) ¹⁴
	$\nu_1(\text{Hg-X})$	$\nu_1(\text{Hg-X})$	$\nu_1(\text{Hg-X})$
	144*	130*	118*
	$\underline{d}(\text{solid})$	$\underline{d}(\text{solid})$	$\underline{d}(\text{solid})$
	2.381(6) ¹¹¹		2.531(3) ¹¹²
SCN	$\underline{d}(\text{solution})$	$\underline{d}(\text{solution})$	$\underline{d}(\text{solution})$
	2.410(2) ^I	2.464(3) ^{IX}	2.547(4) ^{IX}
	$\nu_1(\text{Hg-X})$	$\nu_1(\text{Hg-X})$	$\nu_1(\text{Hg-X})$
	266 ^{IX}	241 ^{IX}	235 ^{IX}

* Ref. 15

4.5.3. The mercury(II), cadmium(II) and zinc(II) thiocyanate complexes

X-ray structure determinations of the $\text{Hg}(\text{SCN})_n^{2-n}$ complexes, $n=1-4$, in DMSO solution have been performed. The complex HgSCN^+ disproportionates, presumably completely, into $\text{Hg}(\text{DMSO})_6^{2+}$ and $\text{Hg}(\text{SCN})_2$ at concentrations $> 0.15-0.20 \text{ M}$ as indicated by raman measurements.^{IV} On the other hand, the other mercury(II) thiocyanate complexes, $\text{Hg}(\text{SCN})_n^{2-n}$, $n = 2-4$, dominate completely in their respective range in concentrated solutions. This applies also to $\text{Hg}(\text{SCN})_3^-$ which in dilute solutions never exceeds 50% of the total mercury concentration.^{II}

The x-ray diffraction measurements show that the Hg-S distances increase with increasing number of thiocyanate ions coordinated to mercury(II). Tables 9 and 10. It was also shown that the Hg-S-C angle in all the studied mercury(II) thiocyanate complexes was about 105° , which is typical for sulfur coordinating thiocyanate complexes.⁶⁰

Raman spectrum of a $0.80 \text{ M Hg}(\text{SCN})_2$ solution shows a weak band at 318 cm^{-1} , which is assigned to $\nu_3(\text{Hg-S})$. The existence of this band indicates that the S-Hg-S angle in the second complex is nonlinear. The third complex, $\text{Hg}(\text{SCN})_3^-$, is found to be almost tetrahedral. A smoothed $\underline{D}(\underline{r})_{\text{obs}} - \underline{D}(\underline{r})_{\text{calc}}$ function, can only be obtained if one DMSO molecule is assumed to be coordinated to mercury at Hg-O and Hg-S distances of 2.7 and 3.7 Å, respectively, which would mean that the DMSO occupies the fourth vertex in a tetrahedron. No S-S distance related to this tetrahedron can be found, however. The refined parameters of the mercury(II) thiocyanate complexes are given in Table 10.

Cadmium(II) forms rather weak complexes with thiocyanate. Even at high concentrations of thiocyanate no complex higher than the third one is formed in the solutions studied.⁸ The radial distribution function shows that cadmium(II) coordinates thiocyanate via the sulfur atom. The Cd-S distance in the solution studied of $\bar{n}=2.3$, is $2.634(11) \text{ Å}$ indicating that the octahedral configuration around cadmium(II) persists¹¹³⁻¹¹⁵ while for the other halides, the second complex is already tetrahedral. This is in agreement with the thermodynamics of the cadmium(II) thiocyanate system in DMSO.^{8,9}

Table 10. Least-squares refinements on the reduced X-ray intensity curves. The parameters describing atomic interactions are: d = distance (Å), b = temperature-factor coefficient (Å²) and n = number of distances per metal atom. The standard deviations given within parentheses for refined parameters is obtained from the least-squares process. The intramolecular intensity contributions from the DMSO molecule and from the ClO₄⁻ ion, if present, were held constant during the refinements.

Solution ^a		ZNNCS4	CDSCN2	HGSCN2	HGSCN3	HGSCN4a	HGSCN4b
Interaction							
M-S	<u>d</u>	4.73(4)	2.634(11)	2.410(2)	2.464(3)	2.547(4)	2.531(7)
	<u>b</u>	0.020	0.010	0.0006(2)	0.0057(4)	0.0037(6)	0.0098(6)
	<u>n</u>	4.0	2.3	2.0	3.0	4.0	4.1(1)
M-C	<u>d</u>	3.07	3.49	3.287(14)	3.35(4)	3.427(14)	3.40
	<u>b</u>	0.013	0.018	0.005	0.010	0.010	0.012
	<u>n</u>	4.0	2.3	2.0	3.0	4.0	4.0
M-N	<u>d</u>	1.93	4.35	4.195	4.236	4.30	4.27
	<u>b</u>	0.007	0.025	0.010	0.018	0.018	0.021
	<u>n</u>	4.0	2.3	2.0	3.0	4.0	4.0
S-S	<u>d</u>				4.02	4.127(16)	4.13
	<u>b</u>				0.004	0.004(2)	0.023
	<u>n</u>				3.0	6.0	6.0
M-O	<u>d</u>		2.30	2.655(5)	2.70		
	<u>b</u>		0.012	0.0085(13)	0.012		
M-S	<u>d</u>		3.43	3.656(5)	3.70		
	<u>b</u>		0.020	0.032(3)	0.022		
M-O and M-S	<u>n</u>		3.7	3.7(3)	1.0		

^a Referred to the solutions in paper IV.

The refined parameter to the cadmium(II) thiocyanate solution studied is given in Table 10.

Zinc(II) forms relatively strong complexes with thiocyanate in

DMSO.¹⁰ The fourth complex was studied in DMSO by x-ray diffraction. The only difference between the radial distribution functions of pure DMSO and a 0.30M $\text{Zn}(\text{NCS})_4^{2-}$ solution in DMSO is a shoulder at about 4.7 Å. Refinements gave a Zn-S distance of 4.73(4) Å which means that zinc(II) coordinates thiocyanate via the nitrogen atom. Assuming the Zn-N-C and the N-C-S angles to be linear, and a N-S distance of 2.80 Å in the thiocyanate ions, the Zn-N bond distance would be ≈ 1.93 Å. This is very close to Zn-N distances in solid zinc(II) isothiocyanate complexes of tetrahedral configuration.^{116,117} The refined parameters of the $\text{Zn}(\text{NCS})_4^{2-}$ complex is given in Table 10.

5. DISCUSSION

5.1. Introduction

Obviously, the interactions between acceptors and donors are very dependent upon the solvent. To bring about a dissolution of ionic compounds, a strong solvation is indeed necessary in order to overcome the lattice free energy. Complex formation means that solvate molecules coordinated to the acceptors are substituted by other ligands. As the ligands are solvated as well, their solvate molecules must be substituted by the acceptor.

The solvation depends on several kinds of intermolecular interactions as ordinary Coloumb interactions,¹¹⁸ hydrogen bonding, covalent interactions and London forces¹¹⁹ not only between the acceptor and the solvent molecules, but also between the solvent molecules. The solvation of acceptors and donors will therefore vary considerably between different solvents. The heats of solvation of the Zn^{2+} , Cd^{2+} and Hg^{2+} , and of their neutral halide complexes in aqueous and DMSO solution have been reported by Ahrland et.al.¹⁷ The solvation enthalpies of these ions are in both aqueous and DMSO solution largest for zinc(II) and smallest for cadmium(II).¹⁷

Zinc(II) and mercury(II) form mainly electrostatic and covalent bonds respectively, while cadmium(II) forms bonds of an intermediate character. The oxygen in DMSO is less hard than in water. This is shown by the transfer enthalpies (water $\rightarrow$ DMSO), that the solvation

of these ions are favoured in DMSO in the order $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. Anions have generally a lower charge density than cations. The halide ions are selectively solvated due to their different hydrogen bonding ability. The capacity for hydrogen bonding decrease in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$, and in water the solvation of the halides sharply decreases in that order. In DMSO, this order is very much levelled. The heats of transfer of the halides from water to DMSO are 19, 4 and -13 kJ mol^{-1} for Cl^- , Br^- and I^- , respectively.¹⁶

When positively charged ions and complexes react with negatively charged ligands, the neutralization of charges causes the solvation of the metal ion to decrease. Consequently the entropy generally gain decreases for each consecutive step. If a change of the coordination figure involving a strong desolvation occurs at a certain step, the enthalpy and entropy changes of this step are markedly more positive than for the other steps.¹⁸

5.2. Thermodynamics and structures of mercury(II) halide and thiocyanate complexes in dimethylsulfoxide solution

Mercury(II) forms very strong complexes with the halides both in aqueous⁹⁴ and DMSO solution.^{II} The complex formation follows a marked (b)-sequence in water and a less marked one in DMSO. In dilute solutions of the mercury(II) halide and thiocyanate systems in DMSO, all complexes, except the third thiocyanate one, successively attain a very large share of the total mercury(II) concentration^{II}. This corresponds to very high values of the ratios K_j/K_{j+1} , $j=1-3$. The thermodynamics of formation of these complexes in DMSO thus follow a pattern which is quite different from that in water. The values of the enthalpy changes, ΔH_j^0 , do not vary much between the ligands, or between the consecutive steps. Table 3 and Fig. 5. This levelling is brought about by a combination of several causes. Firstly, the heat of solvation of the mercury(II) ion is considerably larger in DMSO than in water, which tends to decrease the $-\Delta H_j^0$ value and preferably for the first steps. Secondly, the differences between the heats of solvation of the halide ions are much smaller in DMSO than in water. While the values of ΔH_j^0 thus do not offer much information about the individual complexes

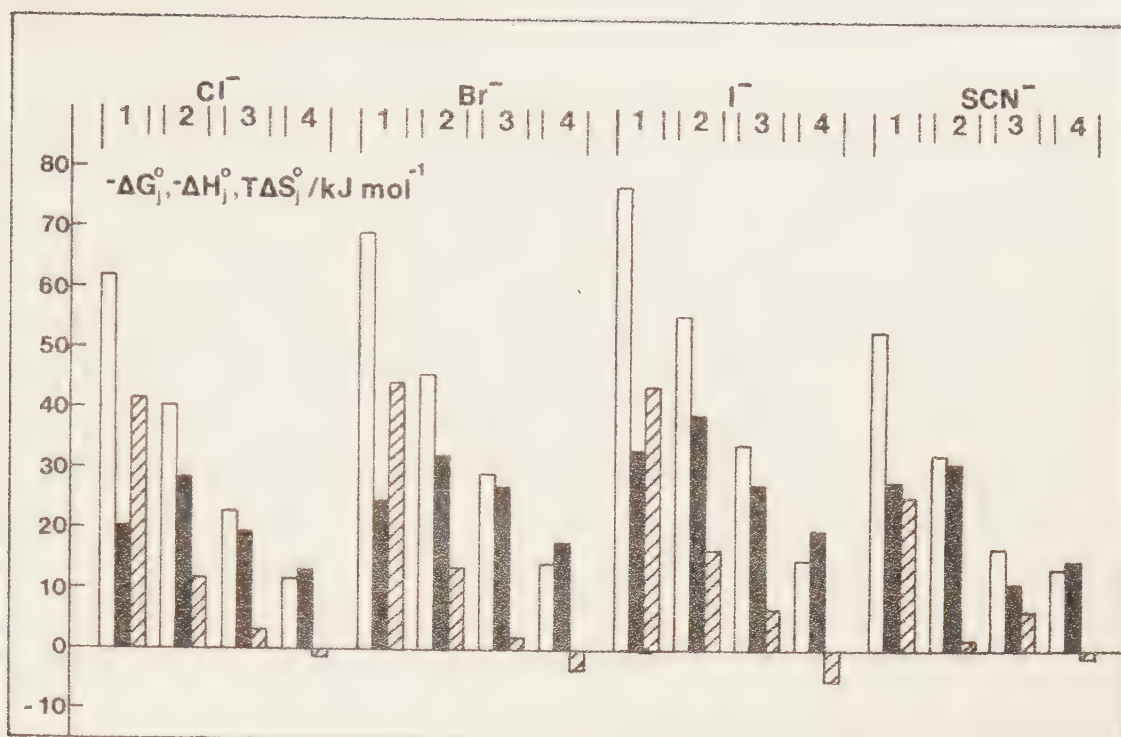


Fig. 5. The changes of free energy (white), enthalpy (black) and entropy (hatched) for the consecutive steps of the mercury(II) halide and thiocyanate systems in DMSO. Medium 1M NH_4ClO_4 , 25°C .

the entropy changes, ΔS_j° , are very informative. The terms which decide the entropy changes are mainly the desolvation of acceptors and donors, and changes of coordination and bond strength when further ligands are coordinated. For all the mercury(II) halide and thiocyanate systems, extremely large positive values of ΔS_1° , clearly show that an extensive desolvation takes place when the first complex is formed. As seen in Fig. 5, these complexes are strongly entropy stabilized. This stabilization prevails only in dilute solutions, however. In more concentrated solutions, HgX^+ disproportionates into $\text{Hg}(\text{DMSO})_6^{2+}$ and HgX_2 in the case of chloride, bromide and thiocyanate and into Hg_2I^{3+} and HgI_2 in the case of iodide. The disproportionation becomes prominent at $C_M \approx 0.1 \text{ M}$ which means that around 150 DMSO molecules per mercury(II) are required, if the entropy stabilization is to persist. The higher complexes of these systems are mainly enthalpy stabilized, Fig. 5. The values of ΔS_2° are still quite large for the halides, indicating

a substantial desolvation when the second complex is formed. The value of ΔS_2^0 for the thiocyanate system is very small, however, indicating that in this case the desolvation accompanying the formation of the second complex is not very extensive. The values of ΔS_3^0 for the halide systems are quite small which would mean that the HgX_2 complexes are relatively weakly solvated. This has been confirmed by determinations of the heats of solvation of the HgX_2 complexes which are only $\approx 5\%$ of the heat of solvation¹⁷ of Hg^{2+} . In the case of the thiocyanate system, the value of ΔS_3^0 is much larger indicating that a relatively strong desolvation takes place when the third mercury(II) thiocyanate complex is formed. From structural investigations in solution, no significant differences are found between the bond distances Hg-DMSO in the complexes $\text{Hg}(\text{SCN})_2$ and HgX_2 , $\text{X}=\text{Cl}$, Br and I . The values of ΔS_4^0 are for all mercury(II) systems investigated slightly negative, indicating a weak solvation of the third complexes. The value turns < 0 , as the tetrahedrons formed represents a high degree of order.

The total entropy changes of the mercury(II) halide and thiocyanate systems are in DMSO of same magnitude as in the corresponding zinc(II) and cadmium(II) systems though the distribution of the entropy changes between the four steps is very different. When the complex formation starts with solvated metal ions and ends with tetrahedral complexes of same structure, the entropy gains are similar, independent of metal ion and halide, Tables 4 and 5.

The complexes HgX_2 are all slightly bent in solution,^{15,112-114} depending on the solvation of the complexes. In the case of the $\text{Hg}(\text{SCN})_2$ complex, the S-S distance could not be found in the radial distribution function, but a $\nu_3(\text{Hg-S})$ frequency is found in the raman spectrum, indicating that also $\text{Hg}(\text{SCN})_2$ is bent^{IX}. The Hg-X distance in HgX_2 $\text{X}=\text{Cl}$, Br , I and SCN are in DMSO slightly longer than in the corresponding solids, Table 9.

The complexes HgX_3^- , $\text{X}=\text{Cl}$, Br , I and SCN , have slightly different structures in DMSO solution.^{IX,14,15} The chloride is trigonally planar and the bromide one a very flat complex pyramid¹⁴. In both complexes, two DMSO are weakly coordinated completing trigonal bipyramids. In HgCl_3^- and HgBr_3^- mercury(II) is thus five-coordinated.

In HgI_3^- and $\text{Hg}(\text{SCN})_3^-$ the ligands are, on the other hand almost in tetrahedral positions,^{IV,14} one DMSO coordinated to mercury in the fourth vertex. In these complexes, mercury is thus four-coordinated. The fourth complexes, HgX_4^{2-} , $\text{X}=\text{Cl}, \text{Br}, \text{I}$ and SCN , are all regular tetrahed ions.^{VIII,IX,14,15}

The Hg-X distances in solid state and DMSO solution and the $\nu_1(\text{Hg-X})$ frequencies of HgX_2 , HgX_3^- and HgX_4^{2-} are in Table 9.

5.3. The influence of medium ions and ionic strength on the complex formation in dimethylsulfoxide solution

The (a)-sequence found for the cadmium(II) halides in 1 M ammonium perchlorate is much more marked in 0.1 M ammonium perchlorate, Table 4. The decrease of the ammonium ion concentration favours the halides in the same order as they are able to form hydrogen bonds, indicating that the halides on account of hydrogen bond formation interact with the ammonium ions. Especially ammonium chloride is markedly associated in DMSO. In the medium 0.1 M tetraethyl-ammonium perchlorate, where little interactions with the halides should take place, the cadmium(II) halide complexes are in fact, as expected, stronger than in the ammonium media, Table 6. The same applies to the lithium and sodium media. In the lithium solutions, however, the pattern of thermodynamics differ markedly from that found for the other media, Table 6. The total entropy gain, $\Delta S_{\beta 4}$, is larger in the lithium media. Even more remarkable, the stepwise ΔS_j^0 show that the switch from octahedral to tetrahedral coordination occurs in the lithium media on the formation of the third complex, but in the other media already on the formation of the second one. The reason for this difference is so far not clear.

The most important change in the thermodynamics when decreasing the ammonium concentration from 1 M to 0.1 M is a larger entropy gain, $\Delta S_{\beta 4}^0$, Tables 4 and 5. This indicates that the ammonium ion has a marked ability to increase the order in the DMSO bulk. This ability decreases in the order $\text{NH}_4^+ > \text{Na}^+ > (\text{C}_2\text{H}_5)_4\text{N}^+$, Table 6.

The differences in the thermodynamics in 1 M and 0.1 M ammonium perchlorate and 1 M sodium perchlorate^{IX} are much the same for the

zinc(II) and cadmium(II) bromide systems. For the zinc(II) system, the enthalpy and entropy changes show that the switch from octahedral and tetrahedral coordination occurs mainly at the first step in 1 M ammonium perchlorate, while it presumably occurs both at the first and the second step in the other media.^{IV}

5.4. The mode of coordination of the thiocyanate ion to zinc(II), cadmium(II) and mercury(II) in dimethylsulfoxide solution

It is shown by raman and x-ray diffraction measurements that zinc(II) coordinates thiocyanate via the nitrogen atom in DMSO solution^{IX}. This is to be expected as the hard zinc(II) ion prefers hard donors, and the nitrogen is the hard end of the thiocyanate ion. In all zinc(II) thiocyanate complexes studied in solution, zinc(II) coordinates thiocyanate through the nitrogen atom, independent of the solvent used.¹²⁰ In solids, the thiocyanate ion is coordinated through nitrogen or acts as a bridge between zinc(II) ions.^{67,121}

For cadmium(II), spectroscopic measurements cannot decide with certainty the mode of coordination of the thiocyanate ion in DMSO^{IX} or aqueous solution⁶⁸. Diffraction measurements show, however, that in DMSO the coordination takes place via sulfur. The Cd-S bond in $\text{Cd}(\text{SCN})_2$ is long, 2.63 Å, which is more than 0.2 Å longer than in corresponding mercury(II) complex.^{IX} The Cd-S bond is thus weak. Consequently, the electron distribution in SCN^- changes only little which is certainly the reason why no information is obtained from the spectroscopic measurements. In many solid cadmium(II) thiocyanate complexes⁶⁷, thiocyanate acts as bridge between cadmium(II) ions. In the compound $\text{Cd}(\text{NCS})_2(\text{s})$, the Cd-N distances are markedly shorter than the Cd-S ones, indicating mainly nitrogen coordination in this compound.¹²² It is surprising that thiocyanate coordination changes, depending upon whether the cadmium(II) ion is solvated or not. In DMSO solution no polynuclear complexes were indicated in the diffraction measurements. Such complexes have however been suggested in aqueous solutions containing a larger excess of cadmium(II)⁶⁸.

In solids, mercury(II) coordinates thiocyanate via sulfur in discrete complexes, but in some cases, the thiocyanate ion acts as bridge between mercury(II) ions.^{67,123} In DMSO solution, thiocyanate



is coordinated through the sulfur atom.^{IX} No polynuclear complex is found in solution. Sulfur coordination is to be expected for the soft acceptor mercury(II) which strongly prefer soft donors and, accordingly, the sulfur atom in thiocyanate.

6. ACKNOWLEDGEMENTS

I am greatly indepted to Professor Sten Ahrland for introducing me to the field of inorganic solution chemistry, for his continous interest and valuable support, for all facilities placed at my disposal and for many stimulating discussions during the course of this work.

I wish to thank Professor Sture Fronæus for his interest and for putting the best working facilities at my disposal.

Many thanks are also due to Dr. Magnus Sandström for introducing me to the field of x-ray diffraction on solutions, Dr. Åke Oskarsson for introducing me to the field of x-ray crystallography and Professor Roberto Portanova, Dr. Eva Hansson and Mr. Åke Iverfeldt for pleasant cooperation and stimulating discussion.

I should also like to thank the following: Britt Ahrland for linguistic revisions, Anna-Lena Augzell, Gunilla Hansson and Elisabeth Nilsson for typing the manuscripts, Lars Seiron for fotografic work, Christina Oskarsson, Ove Hansson and Simon Danielsson for technical assistance.

To all my friends and colleagues, who have helped and supported me in many ways throughout this work, I extend my thanks.

Financial support by the Swedish Natural Science Research Council is hereby gratefully acknowledged.

7. REFERENCES

- 1 Sillén, L.G. and Martell, A.E., Eds., Stability Constants of Metal-Ion Complexes, Chemical Society, Special Publications Nos. 17 and 25, London 1964, 1971.
Högfeldt, E. and Perrin, D.D., Eds., Stability Constants of Metal-Ion Complexes, Pergamon Press, IUPAC Chemical Data Serie Nos. 21 and 22, respectively, Oxford New York Toronto Sydney Paris Frankfurt 1979.
- 2 Ahrland, S., Chatt, J. and Davies, N.R. Quart. Rev. Chem. Soc. 12 (1958) 265
- 3 Pearson, R.G. J. Am. Chem. Soc. 85 (1963) 3533
- 4 Ahrland, S. Struct. Bond. 1 (1966) 207
- 5 Jørgensen, C.K. Struct. Bond. 1 (1966) 234
- 6 Pearson, R.G. J. Chem. Educ. 45 (1968) 581, 643
- 7 Ahrland, S. Struct. Bond. 5 (1968) 118
- 8 Ahrland, S. and Björk, N.O. Acta Chem. Scand. A30 (1976) 249
- 9 Ahrland, S. and Björk, N.O. Acta Chem. Scand. A30 (1976) 257
- 10 Ahrland, S. and Björk, N.O. Acta Chem. Scand. A30 (1976) 265
- 11 Ahrland, S., Björk, N.O. and Portanova, R. Acta Chem. Scand. A30 (1976) 270
- 12 Ohtaki, H., Maeda, M. and Ito, S. Bull. Chem. Soc. Japan 47 (1974) 2217
- 13 Pocev, S., Triolo, R. and Johansson, G. Acta Chem. Scand. A33 (1979) 179
- 14 Gaizer, F. and Johansson, G. Acta Chem. Scand. 22 (1968) 3013
- 15 Sandström, M. Acta Chem. Scand. A32 (1978) 627
- 16 Krishnan, C.V. and Friedman, H.L. J. Phys. Chem. 73 (1969) 3934
- 17 Ahrland, S., Kullberg, L. and Portanova, R. Acta Chem. Scand. A32 (1978) 251

- 18 Ahrland, S. Pure Appl. Chem. 51 (1979) 2019
- 19 Björk, N.O. Thesis, University of Lund, 1975
- 20 Cotton, F.A., Francis, R. and Horrocks Jr., W.D. J. Phys. Chem. 64 (1960) 1534
- 21 Selbin, J., Bull, W.E. and Holmes, Jr., L.H. J. Inorg. Nucl. Chem. 16 (1961) 219
- 22 March, F.C. and Ferguson, G. Can. J. Chem. 49 (1971) 3590
- 23 Mercer, A. and Trotter, J. J. Chem. Soc. Dalton (1975) 2480
- 24 McMillan, R.S., Mercer, A. and Trotter, J. J. Chem. Soc. Dalton (1975) 1006
- 25 Sokol, V.I., Rubtsova, N.D. and Gribenyuk, A.Y. Zh. Strukt. Khim. 15 (1974) 318
- 26 Langs, D.A., Hare, C.R. and Little, R.G. Chem. Commun. (1974) 366
- 27 Bennet, M.J., Cotton, F.A., Weaver, D.L. Williams, R.J. and Watson, W.H. Acta Crystallogr. 23 (1967) 788
- 28 McPartlin, M. and Mason, R. J. Chem. Soc. (1970) 2206
- 29 Melanson, R. and Rochon, F.D. Can. J. Chem. 53 (1975) 2371
- 30 Melanson, R. and Rochon, F.D. Acta Crystallogr. B34 (1978) 941
- 31 Melanson, R. and Rochon, F.D. Inorg. Chem. 17 (1978) 679
- 32 Melanson, R. and Rochon, F.D. Acta Crystallogr. B33 (1977) 3571
- 33 Melanson, R. and Rochon, F.D. Acta Crystallogr. B34 (1978) 1125
- 34 Melanson, R., Hubert, J. and Rochon, F.D. Acta Crystallogr. B32 (1976) 1914
- 35 Björk, N.O. and Cassel, A. Acta Chem. Scand. A30 (1976) 235
- 36 Sandström, M. Acta Chem. Scand. A32 (1978) 527

- 37 Biscarini, P., Fusina, L., Nivellini, G.D., Mangia, A. and Pelizzi, G. J. Chem. Soc. Dalton (1974) 1846
- 38 Bennet, M.J., Cotton, F.A. and Weaver, D.L. Acta Crystallogr. 23 (1967) 581
- 39 Willet, R.D. and Chang, K. Inorg. Chim. Acta 4 (1970) 447
- 40 Willet, R.D., Jardine, F.J. and Roberts, S.A. Inorg. Chim. Acta 25 (1977) 97
- 41 Williams, R.J., Watson, W.H. and Larson, A.C. Acta Crystallogr. B31 (1975) 2362
- 42 Ferguson, J.E., Page, C.T. and Robinson, W.T. Inorg. Chem. 15 (1976) 2270
- 43 Sandström, M. Acta Chem. Scand. A32 (1978) 519
- 44 Lindqvist, I., Inorg. Adduct Molecules of Oxo-Compounds, Springer, Verlag, Berlin, 1963, p. 73
- 45 Aslanov, L.A., Ionov, V.M., Attiya, V.M. Permin, A.B. and Petrosyn, V.S. Zh. Strukt. Khim. 19 (1978) 109
- 46 Coghi, L., Nardelli, M., Pelizzi, C. and Pelizzi, G. Gazz. Chim. Ital. 105 (1975) 1187
- 47 Coghi, L., Pelizzi, C. and Pelizzi, G. Gazz. Chim. Ital. 104 (1974) 873
- 48 Coghi, L., Pelizzi, C. and Pelizzi, G., J. Organomet. Chem. 114 (1976) 53
- 49 Isaacs, N.W. and Kennard, C.H.L. J. Chem. Soc. A (1970) 1257
- 50 Bhandary, K.K. and Manohar, H. Acta Crystallogr. B29 (1973) 1093
- 51 Aslanov, L.A., Soleva, L.I., Porai-Koshits, M.A. and Goukberg, S.S. Zh. Strukt. Khim. 13 (1972) 655
- 52 Aslanov, L.A., Soleva, L.I. and Porai-Koshits, M.A. Zh. Strukt. Khim. 13 (1972) 1101
- 53 Bhandary, K.K., Manohar, H. and Venkatesan, K. J. Chem. Soc. Dalton (1975) 288

- 54 Aslanov, L.A., Soleva, L.I. and Porai-Koshits, M.A.
Zh. Strukt., Khim. 14 (1973) 1064
- 55 Baranyi, A.D., Onyszchuk, M., Fortier, S. and Donnay, G.
J. Chem. Soc. Dalton (1976) 2301
- 56 Baranyi, A.D., Onyszchuk, M., Le Page, Y. and Donnay, G.
Can. J. Chem. 55 (1977) 849
- 57 Singer, N. and Studd, B.F. J. Chem. Soc. D (1970) 342
- 58 Bombeiri, G. and Bagnall, K. J. Chem. Soc. Chem. Comm.
(1975) 188
- 59 Dewan, J.C., Edwards, A.J., Slim, D.R., Guerchais, J.E.
and Kergoat, R. J. Chem. Soc. Dalton (1975) 2171
- 60 Viswamitra, M.A. and Kannan, K.K. Nature 209 (1966) 1016
- 61 Reynolds, W.L., In Lippard, S.J., Ed., Progress in In-
organic Chemistry, Interscience, New York, London, Sydney,
Toronto 1970, Vol. 12, Chapter 1
- 62 Ahrland, S. and Björk, N.O. Acta Chem. Scand. A28 (1974)
823
- 63 Christensen, J.J., Ruckman, J., Eatough, D.J. and Izatt,
R.M. Thermochim. Acta 3 (1972) 203
- 64 Saimoilenko, V.M. and Lyashenko, V.I. Russ. J. Inorg.
Chem. 18 (1973) 1578
- 65 Sandström, M. and Johansson, G. Acta Chem. Scand. A31
(1977) 132
- 66 Sandström, M. Acta Chem. Scand. A31 (1977) 140
- 67 Norbury, A.H., In Advances in Inorganic Chemistry and
Radiochemistry, Academic Press New York San Francisco
London, Vol. 17, p. 231, 333
- 68 Fronæus, S. and Larsson, R. Acta Chem. Scand. 16 (1962)
1447
- 69 Persson, H. Acta Chem. Scand. 24 (1970) 3739
- 70 Grenthe, I., Ots, H. and Ginstруп, O. Acta Chem. Scand.
24 (1970) 1067

- 71 Ots, H. Acta Chem. Scand. 26 (1972) 3810
- 72 Wagman, D.D., Bailey, S.M. and Schumm, R.H. Selected Values of Chemical Thermodynamic Properties, N.B.S. Technical Note 270 - 3 Jan. 1968
- 73 Rossini, F.D. Selected Values of Chemical Thermodynamic Properties, U.S. Government Printing office, Washington, 1952
- 74 Karlsson, R. and Kullberg, L. Chem. Scr. 9 (1976) 54
- 75 Svensson, C. Thesis, Institute of Technology, Lund 1978
- 76 Syntex Analytical Instruments, Inc., 10040 Bubb Road, Cupertino, Ca 95014, USA
- 77 Johansson, G. and Sandström, M. Chem. Scr. 4 (1973) 195
- 78 International Tables of X-Ray Crystallography, Vol. 3 and 4, Kynoch Press, Birmingham 1968 and 1974, respectively
- 79 Stewart, R.F., Davidson, E.R. and Simpson, W.T. J. Chem. Phys. 42 (1965) 3175
- 80 Cromer, D.T. Acta Crystallogr. 18 (1965) 17
- 81 Cromer, D.T. and Mann, J.B. J. Chem. Phys. 47 (1967) 1892
- 82 Cromer, D.T. J. Chem. Phys. 50 (1969) 4857
- 83 Compton, A.H. and Allison, S.K. X-Rays in Theory and Experiment, van Nostrand, New York 1935
- 84 Breit, G. Phys. Rev. 27 (1926) 362
- 85 Dirac, P.A.M. Proc. R. Soc. London A111 (1926) 405
- 86 Dwigings, C.W. and Park, D.A. Acta Crystallogr. A27 (1971) 264
- 87 Levy, H.A., Danford, M.D. and Narten, A.H. Data Collection and Evaluation with an X-Ray Diffractometer Designed for the Study of Liquid Structure, Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge 1966
- 88 Åhrland, S., Bläuenstein, P., Tagesson, B. and Tuhtar, D. To be published

- 89 Ahrland, S. and Rawsthorne, J. Acta Chem. Scand. 24 (1970)
- 90 Handbook of Chemistry and Physics, Chemical Rubber Co. Press, 58th Ed. 1977-1978
- 91 Hedwig, G.R., Owensby, D.A. and Parker, A.J. J. Am. Chem. Soc. 97 (1975) 3888
- 92 Persson, I. and Marton, A. To be published
- 93 Gupta, A.K. J. Chem. Soc. (1952) 3473
- 94 Sillén, L.G. Acta Chem. Scand. 3 (1949) 539
- 95 Marcus, Y. Acta Chem. Scand. 11 (1957) 599
- 96 Gallagher, P.K. and King, E.L. J. Am. Chem. Soc. 82 (1960) 3510
- 97 Björkman, M. and Sillén, L.G. Trans. Royal Inst. Technol. Stockholm (1963) No 199
- 98 Christensen, J.J., Izatt, R.M., Hansen, L.D. and Hale, J.D. Inorg. Chem. 3 (1964) 130
- 99 Ahrland, S. and Kullberg, L. Acta Chem. Scand. 25 (1971) 3692
- 100 Clarke, J.H.R. and Woodward, L.A. Trans. Faraday Soc. 61 (1965) 207
- 101 Ferguson, G., Jeffreys, J.A.D. and Sim, G.A. J. Chem. Soc. B (1966) 454
- 102 Clegg, W., Brown, M.L. and Wilson, L.J.A. Acta Crystallogr. B32 (1976) 2905
- 103 Kamenar, B. and Nagl, B. Acta Crystallogr. B32 (1976) 1414
- 104 Stålhandske, C.I. Personal communication
- 105 Sandström, M. and Liem, D.H. Acta Chem. Scand. A32 (1978) 509
- 106 Leligny, H., Frey, M. and Monier, J.C. Acta Crystallogr. B28 (1972) 2104

- 107 White, J.G. Acta Crystallogr. 16 (1963) 397
- 108 Jeffrey, G.A. and Vlasse, M. Inorg. Chem. 6 (1967) 396
- 109 Gerken, V.A. and Pakhomov, V.I. Zh. Strukt. Khimii 10 (1969) 753
- 110 Pakhomov, B.I., Fedorov, P.M., Alymov, I.M., Ivanova-Korfini, I.N. and Semin, G.K. Izv. Akad. Nauk. SSSR ser. Fiz. 39 (1975) 2519 and references therein
- 111 Beauchamp, A.L. and Goutier, D., Can. J. Chem. 50 (1972) 977
- 112 Sakhri, A. and Beauchamp, A.L. Acta Crystallogr. A31 (1975) 409
- 113 Cavalca, L., Domiano, P., Fava Gaspani, G. and Boldrini, P. Acta Crystallogr. 22 (1967) 878
- 114 Cavalco, L., Nardelli, M. and Fava, G. Acta Crystallogr. 13 (1960) 125
- 115 Guseinov, G.D., Guesinov, G.G., Ismailov, M.Z. and Godžaez, E.M. Izv. Akad. Nauk. SSSR, Neorg. Materialy 5 (1969) 33
- 116 Bigoli, F., Braibanti, A., Pellinghelli, M.A. and Tiripicchio, A. Acta Crystallogr. B29 (1973) 2708
- 117 Caira, M. and Nassimbeni, L.R. Cryst. Struct. Commun. 5 (1976) 309
- 118 Schwarzenbach, G. Pure Appl. Chem. 24 (1970) 307
- 119 Ahrland, S. In J.J. Lagowski, Ed., The chemistry of Non-Aqueous Solvents, Academic Press New York San Francisco London, 1978, Vol. VA, Chapter 1
- 120 Stommen, D.P. and Plane, R.P. J. Chem. Phys. 60 (1974) 2463 and references therein
- 121 Aslanov, L.A., Ionov, V.M. and Kynev, K. Kristallografija 21 (1975) 1198
- 122 Cannas, M., Carta, G., Cristini, A. and Marongiu, G. J. Chem. Soc. Dalton (1976) 300

- 123 Sakhri, A. and Beauchamp, A.L. Inorg. Chem. 14 (1975) 740
- 124 Davies, A.R., Einstein, F.W.B., Farrell, N.P., James, B.R.
and McMillan, R.S. Inorg. Chem. 17 (1978) 1965

Correspondance and proofs should be sent to:

Fil.kand. Ingmar Persson, Oorganisk kemi 1, Kemicentrum,
Lunds Universitet, Box 740, S-220 07 Lund 7, Sverige.

Running Titles: Ahrland and Persson

Metal Complexes in DMSO VIII

Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide Solution VIII. Standard Electrode Potentials in Dimethylsulfoxide Solution and Exchange Reactions between Dimethylsulfoxide and Water. Involving Metal Ions of Groups 1 b and 2 b.

STEN AHRLAND and INGMAR PERSSON

Inorganic Chemistry 1, Chemical Center, University of Lund,
P.O. Box 740, S-220 07 Lund 7, Sweden.

Standard electrode potentials have been calculated for zinc, cadmium, mercury and copper couples in dimethylsulfoxide, on the extrathermodynamic assumption that the standard potential of the silver couple is 349 mV more negative in DMSO than in water. All the metals concerned are much less noble in DMSO than in water, i.e. the transfer free energies $\Delta G_{tr}^0 < 0$. For those ions where they have been determined, the transfer enthalpies ΔH_{tr}^0 are even more negative, however, so the transfer entropies $\Delta S_{tr}^0 < 0$. This ions are thus more easily solvated by DMSO than by water, and their transfer to DMSO means an increase of the overall order of the system. The preference for DMSO among the ions investigated follows the order $Zn^{2+} < Cu^{2+} < Cd^{2+} < Hg_2^{2+} < Ag^+ \approx Hg^{2+} < Cu^+$. This is on the whole their order of softness, with the exeception of Cu^+ whose preference to DMSO is stronger than would be expected.

The electrode potentials of redox couples involving metal ions (as always referred to a certain standard electrode) are apt to change considerably between different solvents. For obvious reasons, by far the largest number of potential measurements refer to aqueous solutions. It is therefore natural to choose water as a solvent of reference. In the following, the changes of electrode potentials accompanying the transfer of a number of important redox couples from water to the aprotic solvent dimethylsulfoxide (DMSO) will be discussed.

Any aprotic solvent to be used for such a comparison must evidently be a strongly solvating one, in order to dissolve the ionic compounds involved. In the present study, DMSO has been chosen, much because measurements referring to zinc, cadmium and copper couples have already been performed in this solvent^{1,2}. Moreover, a study of the mercury couples has been a necessary preliminary to an investigation of the mercury(II) halide and thiocyanate complexes formed in DMSO solution³.

To relate electrode potentials measured in different solvents, an extrathermodynamic assumption must be introduced^{4,5}. The approach nearest to hand is evidently to postulate that the liquid junction potential between two solvents can be suppressed by an appropriate choice of salt bridge^{5,6}. The electrode potential differences arrived at in this way also agree fairly well with those resulting from other reasonable approaches⁵. Among these, however, the modified Grunwald assumption that the free transfer energies ΔG_{tr}^0 between two solvents are the same for the tetraphenylarsonium (Ph_4As^+) and the tetraphenylborate (Ph_4B^-) ions, has lately been generally accepted to be closest to the truth⁷⁻⁹. This assumption will therefore be adopted here. An additional reason for doing so is that the single ion enthalpies of transfer used in the present study have been calculated on this assumption^{9,10}.

The electrodes actually used in the present potential measurements in DMSO have been Ag/Ag^+ , $\text{Zn}(\text{Hg})/\text{Zn}^{2+}$, $\text{Cd}(\text{Hg})/\text{Cd}^{2+}$, $\text{Hg}/\text{Hg}_2^{2+}$ and $\text{Hg}_2^{2+}/\text{Hg}^{2+}$. The temperature has been 25°C.

The couple Ag/Ag^+ has been thoroughly studied in a large variety of solvents, and in the presence of a large variety of anions^{6,7}. From the solubility products found, reliable values of $\Delta G_{\text{tr}}^{\circ}(\text{Ag}^+)$ between numerous pairs of solvents can be calculated, on the assumption that $\Delta G_{\text{tr}}^{\circ}(\text{Ph}_4\text{As}^+) = \Delta G_{\text{tr}}^{\circ}(\text{Ph}_4\text{B}^-)$ ^{7,11}. Consequently, the electrode potentials of Ag/Ag^+ in any solvent investigated can be related to the reference solvent water. In the following, Ag/Ag^+ in water is chosen as the standard electrode, i.e. $E_{\text{Ag}}^{\circ}(\text{aq}) = 0$. The value of $\Delta G_{\text{tr}}^{\circ}(\text{Ag}^+)$ between water and DMSO is^{7,11} -33.7 kJ/mol at 25°C which means that the standard potential in DMSO, referred to $E^{\circ}(\text{aq}) = 0$ is $E^{\circ}(\text{DMSO}) = \Delta G_{\text{tr}}^{\circ}/nF = -349 \text{ mV}$. Silver is thus a considerably less noble metal in DMSO than in water.

The other couples investigated in DMSO have been determined relative to Ag/Ag^+ . In the case of zinc and cadmium, the two-phase amalgams used attain equilibrium potentials much more quickly and reliably than do the pure metals. As the potential differences between amalgam and metal electrodes are well known, the standard potentials $E_{\text{Zn}}^{\circ}(\text{DMSO})$ and $E_{\text{Cd}}^{\circ}(\text{DMSO})$ of the couples Zn/Zn^{2+} and Cd/Cd^{2+} can be immediately calculated from the present measurements. In the case of mercury, $E_{\text{Hg}}^{\circ}(\text{DMSO})$ of the couple Hg/Hg^{2+} cannot be determined directly, on account of the reprecipitation equilibrium $\text{Hg}(\text{l}) + \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+}$ which is situated rather far to the right. Both this potential and also the equilibrium constant $K_{\text{R}} = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$ can be calculated from the standard potentials of the couples $\text{Hg}/\text{Hg}_2^{2+}$ and $\text{Hg}_2^{2+}/\text{Hg}^{2+}$, however, according to the formulas $E_{\text{O}_2}^{\circ} = (E_{12}^{\circ} + E_{01}^{\circ})/2$ and $\log K_{\text{R}} = (E_{12}^{\circ} - E_{01}^{\circ})/(RT \ln 10/F)$. The difference $E_{12}^{\circ} - E_{01}^{\circ}$, and consequently K_{R} , are of course independent of the extrathermodynamic assumption introduced. The value of K_{R} can also be checked by direct analysis of solutions in equilibrium (see "Experimental").

The measurements in DMSO have been performed in two different media, of the ionic strength $I = 0.15$ and 1 M , in both cases brought about by ammonium perchlorate. The value of $\Delta G_{\text{tr}}^{\circ}(\text{Ag}^+)$ quoted above does not refer to any of these standard states, but rather to the transfer between the pure solvents⁷. Considering the limited accuracy of $\Delta G_{\text{tr}}^{\circ}$ and the rather small difference in E° found for most couples measured between the two DMSO media

employed, Table 1, the difference in standard state is of minor importance. For the other metal ions studied, the values of ΔG_{tr}° to be discussed below refer to the DMSO solution of $I = 1$ M, i.e. they have been calculated according to $\Delta G_{tr}^{\circ} = n F [E^{\circ}(\text{DMSO}, I=1) - E^{\circ}(\text{aq})]$.

An important reason for the large negative values of ΔG_{tr}° found for most ions on transfer from water to DMSO is the large changes in the solvation of the metal ions involved. These changes are reflected in large differences between water and DMSO in the enthalpies of solvation, denoted ΔH_W° and ΔH_D° , respectively. The enthalpies of transfer, $\Delta H_{tr}^{\circ} = \Delta H_D^{\circ} - \Delta H_W^{\circ}$ will thus be considerable. They differ appreciably between various ions, however¹². Among the ions presently discussed, they are well established¹⁰⁻¹³ for Ag^+ , and also for Zn^{2+} , Cd^{2+} and Hg^{2+} .

Due to intermolecular hydrogen bonding, the protic solvent water is much more structured than the aprotic solvent DMSO. Consequently, a transfer of metal ions from water to DMSO is likely to bring about a sizable net increase of order, which tends to make the entropy changes ΔS_{tr}° negative. Also other sources of considerable entropy changes are likely to exist. Generally, both ΔH_{tr}° and ΔS_{tr}° should therefore contribute appreciably to ΔG_{tr}° , and hence to the change of E° between the two solvents. The metal ions so far studied do behave as expected in these respects^{11,13}.

Independent of the extrathermodynamic assumption applied, i.e. of the values of ΔG_{tr}° (i.e. $E^{\circ}(\text{aq}) - E^{\circ}(\text{DMSO})$) chosen, the free energy changes ΔG_{ex}° of the exchange reactions $M_{II}^{n+}(\text{DMSO}) + n/p M_I^{p+}(\text{aq}) \rightleftharpoons M_{II}^{n+}(\text{aq}) + n/p M_I^{p+}(\text{DMSO})$ can be calculated. Consistent with the present choice of standard electrode, Ag^+ is chosen as the reference ion M_I^{p+} so the reactions considered are $M^{n+}(\text{DMSO}) + n \text{Ag}^+(\text{aq}) \rightleftharpoons M^{n+}(\text{aq}) + n \text{Ag}^+(\text{DMSO})$. From the values of ΔG_{ex}° of these reactions, the values of any other combination of ions can be immediately calculated. The differences $\Delta E^{\circ}(\text{aq}) = E_{\text{Ag}}^{\circ}(\text{aq}) - E_M^{\circ}(\text{aq})$ and $\Delta E^{\circ}(\text{DMSO}) = E_{\text{Ag}}^{\circ}(\text{DMSO}) - E_M^{\circ}(\text{DMSO})$ measured in water and DMSO, respectively, evidently do not depend upon ΔG_{tr}° . The emf of a cell with the cell reaction written above is, however, $\Delta E^{\circ} = \Delta E^{\circ}(\text{aq}) - \Delta E^{\circ}(\text{DMSO})$, and hence $\Delta G_{ex}^{\circ} = - n F \Delta E^{\circ}$. Also for the

calculation of $\Delta G_{\text{ex}}^{\circ}$, the standard states chosen are water, $I = 0$, and DMSO, $I = 1$ M.

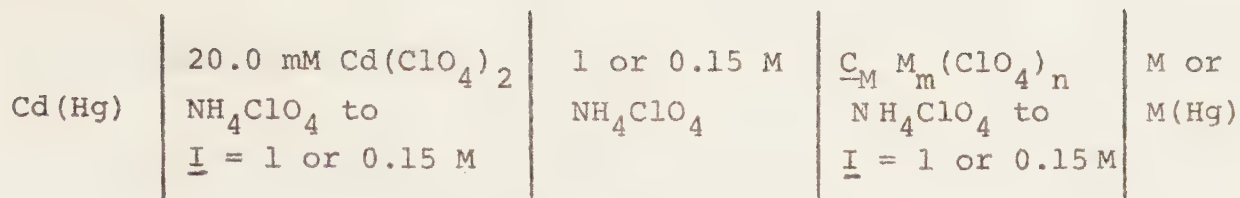
In those cases where $\Delta H_{\text{tr}}^{\circ}$ is known for the ion M^{n+} participating in the exchange, i.e. for Zn^{2+} , Cd^{2+} and Hg^{2+} , the enthalpy change of the reaction can be calculated according to $\Delta H_{\text{ex}}^{\circ} = n\Delta H_{\text{tr}}^{\circ}(\text{Ag}^{+}) - \Delta H_{\text{tr}}^{\circ}(M^{n+})$. Provided that $\Delta H_{\text{tr}}^{\circ}(\text{Ag}^{+})$ and $\Delta H_{\text{tr}}^{\circ}(M^{n+})$ have been calculated on the same extrathermodynamic assumption, as is the case here, the difference in the right membrum, i.e. $\Delta H_{\text{ex}}^{\circ}$ will be independent of this assumption, just as $\Delta G_{\text{ex}}^{\circ}$. For those reactions where $\Delta H_{\text{ex}}^{\circ}$ can be found it is finally also possible to calculate the entropy change $\Delta S_{\text{ex}}^{\circ} = (\Delta H_{\text{ex}}^{\circ} - \Delta G_{\text{ex}}^{\circ})/T$.

EXPERIMENTAL

Chemicals. The solvates $\text{Zn}(\text{DMSO})_6(\text{ClO}_4)_2$, $\text{Cd}(\text{DMSO})_6(\text{ClO}_4)_2$ and $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$, used as sources for the respective metal ions, were prepared and analyzed as before^{14,15}. Anhydrous AgClO_4 was the source of Ag^{+} . A mercury(I) DMSO-solvate, $\text{Hg}_2(\text{ClO}_4)_2 \cdot 3\text{DMSO}$, was prepared as follows, cf.¹⁶. The hydrate $\text{Hg}_2(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$ (0.05 mol) was dissolved in methanol (30 ml). To prevent hydrolysis, the methanol was acidified with a few drops of concentrated perchloric acid. DMSO (0.10 mol) was added. On cooling to 5°C , the DMSO solvate precipitated. It was recrystallized from methanol. The mercury content was determined by titration with cerium(IV)¹⁷; found 48.24, calc. 48.08%. Carbon and hydrogen were determined conventionally^{*}; found 8.77, 2.09; calc. 8.63, 2.17%. Sulfur could not be determined on account of the formation of slightly soluble Hg_2SO_4 . The amalgams were prepared and stored as described previously¹⁸.

Procedure. In practice, a $\text{Cd}(\text{Hg})/\text{Cd}^{2+}$ half-cell was always used as a common reference electrode. The cells measured were thus either

* Analyses performed by the Department of Analytical Chemistry of this Chemical Center.



where $M = \text{Zn}(\text{electrode Zn(Hg)}; m = 1, n = 2)$, $\text{Hg} (m = n = 2)$ or $\text{Ag}(m = n = 1)$, or the right hand half-cell was a Pt-electrode in a solution of $\underline{C}_M \text{ M Hg}_2(\text{ClO}_4)_2$ and $\underline{C}_N \text{ M Hg}(\text{ClO}_4)_2$. For the first type of cells stable emfs, generally reproducible within $\pm 0.1 \text{ mV}$, were reached in a few minutes within the range of concentrations used, $3 \text{ mM} < \underline{C}_M < 50 \text{ mM}$. For the mercury(I) - mercury(II) electrode, reproducible equilibrium potentials were rapidly attained only if $\underline{C}_N \gtrsim \underline{C}_M$, and moreover $\underline{C}_N \gtrsim 15 \text{ mM}$. For all the systems, the emfs measured obey Nernst's law within $\pm 0.3 \text{ mV}$.

The difference in potential between the amalgam and the metal electrode is for Cd 50.5 mV while for Zn no difference seems to exist^{19,20}.

Determination of K_R . The most precise value of K_R is obtained from the potentiometric measurements, as described above. A valuable check is possible, however, by analysis of solutions containing Hg(II) and Hg(I) in equilibrium with metallic mercury. The equilibrium was approached from both sides, either by shaking the metal with a mercury(II) perchlorate solution, or by dissolving $\text{Hg}_2(\text{ClO}_4)_2 \cdot 3\text{DMSO}$, in the appropriate ionic medium. When equilibrium had been reached, the metal was filtered off. The total concentration of mercury in this solution, $\underline{C}_e$, was determined by EDTA-titration²¹, after oxidation of the mercury(I) present by boiling with 5 M nitric acid. At equilibrium, $\underline{C}_e = [\text{Hg}^{2+}]_e + 2[\text{Hg}_2^{2+}]_e$. If $\underline{C}_{\text{II}}$ and $\underline{C}_{\text{I}}$ denote the initial concentration of mercury(II) and mercury(I), respectively, in the two experiments, the following stoichiometric conditions are valid: $\underline{C}_{\text{II}} = [\text{Hg}^{2+}]_e + [\text{Hg}_2^{2+}]_e$; $\underline{C}_{\text{I}} = 2[\text{Hg}_2^{2+}]_e + 2[\text{Hg}^{2+}]_e$. Hence the following expressions for K_R are obtained in the two cases: $K_R = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}] = (\underline{C}_e - \underline{C}_{\text{II}})/(2\underline{C}_{\text{II}} - \underline{C}_e)$ and $K_R = (2\underline{C}_e - \underline{C}_{\text{I}})/2(\underline{C}_{\text{I}} - \underline{C}_e)$.

MEASUREMENTS AND RESULTS

The standard electrode potentials computed from the present measurements, and referred to $\underline{E}_{\text{Ag}}^{\circ}(\text{aq}) = 0$, are listed in Table 1. Also the potentials of the various copper couples, recalculated on the present scale from values determined previously², have been introduced. For these couples, the medium of lower ionic strength had $\underline{I} = 0.1 \text{ M}$, instead of $\underline{I} = 0.15 \text{ M}$ used presently. This difference should not mean a very great change in $\underline{E}^{\circ}(\text{DMSO})$. For comparison, the Table 1 also contains the values²² of $\underline{E}^{\circ}(\text{aq})$ on the same scale. The values of $\underline{E}^{\circ}(\text{DMSO})$ referring to $\underline{I} = 1 \text{ M}$, and of $\underline{E}^{\circ}(\text{aq})$, $\underline{I} = 0$, have been entered in Fig 1.

The values of $\underline{\Delta G}_{\text{tr}}^{\circ}$ calculated from the standard potentials of Table 1 have been listed in Table 2. In so far as values of the enthalpies of transfer, $\underline{\Delta H}_{\text{tr}}^{\circ}$, are known^{10,11,13}, these have been introduced and hence the entropies of transfer calculated according to $\underline{\Delta S}_{\text{tr}}^{\circ} = (\underline{\Delta H}_{\text{tr}}^{\circ} - \underline{\Delta G}_{\text{tr}}^{\circ})/\underline{T}$.

The values of $\underline{\Delta G}_{\text{ex}}^{\circ}$ for the exchange between water and DMSO of Ag^+ for other ions M^{n+} have been listed in Table 3. As no extrathermodynamic assumption is involved, these values are more precise, and certainly also more accurate, than those determined for $\underline{\Delta G}_{\text{tr}}^{\circ}$. The corresponding equilibrium constants, $\underline{K}_{\text{ex}}$, have also been calculated, from $\log \underline{K}_{\text{ex}} = -\underline{\Delta G}_{\text{ex}}^{\circ}/RT \ln 10$. For the reactions involving Zn^{2+} , Cd^{2+} and Hg^{2+} it has also, as discussed above, been possible to calculate the enthalpy changes $\underline{\Delta H}_{\text{ex}}^{\circ}$, and hence also the entropy changes $\underline{\Delta S}_{\text{ex}}^{\circ}$.

The values of the reproporationation constant $\underline{K}_{\text{R}}$ found potentiometrically and by chemical analysis of equilibrium solutions have been entered in Table 4. To ensure a direct comparison with the result of an earlier investigation (see Discussion), $\underline{K}_{\text{R}}$ has also been determined in $0.15 \text{ M Et}_4\text{NClO}_4$ (by shaking mercury(II) with metallic mercury). A value found earlier in a DMSO-NaClO_4 medium is also given²³. For comparison, values of $\underline{K}_{\text{R}}$ determined in water for media of the same ionic strength as used in the present study have also been entered, as well as the value exptropolated for $\underline{I} = 0$ ²⁴.

Already the low values of $\underline{K}_R$ in DMSO are more precisely determined potentiometrically than by chemical analysis; in water the potentiometric method is the best by far.

DISCUSSION

All the metals concerned are considerably less noble in DMSO than in water, as is evident from Table 1 and Fig 1. The difference $\underline{E}^O(\text{aq}) - \underline{E}^O(\text{DMSO})$ is quite large for all the metal electrodes. For ions M^{2+} it clearly increases with increasing softness, being 244, 290 and 352 mV for Zn^{2+} , Cd^{2+} , and Hg^{2+} , respectively. Also Cu^{2+} , with 251 mV, fits fairly well into this order, which would indicate that the solvate bonds are of a more electrostatic character in DMSO than in water.

As stated above these values are all based on a difference for Ag^+ of 349 mV. Rather surprisingly, that of Cu^+ is even higher, 409 mV, though Cu^+ generally behaves as a less soft acceptor than Ag^+ .

These differences are immediately connected with $\underline{\Delta G}_{\text{tr}}^O/n$ i.e. the free energy of transfer per ionic charge. This quantity is thus exceptionally high for Cu^+ . As a consequence, the reaction $\text{Cu}(\text{s}) + \text{Cu}^{2+} \rightarrow 2 \text{Cu}^+$, where 2 Cu^+ is formed for each Cu^{2+} disappearing, is very much favoured in DMSO relative to water². The value of $\underline{K}_R = [\text{Cu}^+]^2/[\text{Cu}^{2+}]$ increases by a factor $10^{5.6}$, corresponding to a free energy change $\underline{\Delta G}^O = 2 \underline{\Delta G}_{\text{tr}}^O(\text{Cu}^+) - \underline{\Delta G}_{\text{tr}}^O(\text{Cu}^{2+}) = -32 \text{ kJ mol}^{-1}$ (Table 2). As a consequence, Cu^+ becomes a fairly stable species in DMSO, the value of $\underline{K}_R (= 1/\underline{K}_D)$ being 0.23 M in 1 M and 0.66 M in 0.1 M NH_4ClO_4 , respectively².

On the other hand, the values of $\underline{E}^O(\text{aq}) - \underline{E}^O(\text{DMSO})$, or $\underline{\Delta G}_{\text{tr}}^O$, are not very different for Hg_2^{2+} and Hg^{2+} , Table 1 and 2. Consequently, $\underline{K}_R$ of the reproporationation $\text{Hg}(\text{l}) + \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+}$ does not change much between water and DMSO, Table 4. For this system, the transfer to DMSO means a slight stabilization of the divalent state relative to the monovalent one. The difference between the two solvents is

so small, however, that a change of medium may bring about effects of the same order of magnitude, Table 4.

These results are throughout compatible with those found earlier²³ for the medium 1 M NaClO₄ but they differ profoundly from the conclusions arrived at in another investigation²⁵. In this study, a large stabilization of Hg₂²⁺ relative to Hg²⁺ is found on the transfer from water to DMSO. That this in fact does not occur is evident not only from the present measurements, but also from the potentiometric determinations of the equilibrium constants of the mercury(II) halide systems recently performed³. These would not have been at all possible, had a strong stabilization of Hg₂²⁺ relative to Hg²⁺ taken place. The reason for the discrepancy may be that the polarographic technique employed does not yield true equilibrium potentials and/or that the indirect determination of E_{02}^O via the gold electrode does not work properly.

The contributions of ΔH_{tr}^O and ΔS_{tr}^O to ΔG_{tr}^O also show very interesting trends, Table 2. For the monovalent Ag⁺, ΔS_{tr}^O is much more negative than for the divalent ions, indicating that the increase of order accompanying a transfer is by far most marked for Ag⁺. While Ag⁺ is poorly solvated in water, the solvation in DMSO is very markedly better. This is also reflected in the high value $\Delta H_{tr}^O/n$, the transfer enthalpy per ionic charge. For the divalent ions, both ΔH_{tr}^O and ΔS_{tr}^O becomes more favourable from Zn²⁺ to Hg²⁺. As to ΔH_{tr}^O , the trend is easily rationalized by postulating that the more covalent character of the solvate bonds in DMSO favours the acceptors more, the softer they are. The values of ΔH_{tr}^O (Hg²⁺) and ΔH_{tr}^O (Ag⁺) are thus large for the same reason. The trend in ΔS_{tr}^O cannot, of course, be interpreted along these lines. The most likely reason might be that the sterical restrictions which must be severe for the DMSO hexasolvates nevertheless are relaxed with increasing radius of the acceptor ion.

The thermodynamics of the exchange reaction reflects the conditions just discussed, Table 3. The transfer of Ag⁺ from water to DMSO, in exchange for the other metal ions concerned, has $\Delta G_{ex}^O < 0$,

except for Hg^{2+} , where it ≈ 0 and for Cu^+ , where $\Delta G_{\text{ex}}^{\circ} > 0$. The values of $\Delta H_{\text{ex}}^{\circ}$, known for Zn^{2+} , Cd^{2+} , Hg^{2+} , in all cases strongly favour the exchange. The values of $\Delta S_{\text{tr}}^{\circ}$ are on the other hand all very unfavourable, for Hg^{2+} to such a degree that the strongly exothermic $\Delta H_{\text{tr}}^{\circ}$ is just compensated.

Acknowledgements: The support given to this investigation by the Swedish Natural Science Research Council is gratefully acknowledged.

REFERENCES

1. Ahrland, S. and Björk, N.-O. Acta Chem. Scand. A 30 (1976) 265.
2. Ahrland, S., Bläuenstein, P., Tagesson, B. and Tuhtar, D. Acta Chem. Scand. In press.
3. Ahrland, S., Persson, I. and Portanova, R. To be published.
4. Strehlow, H. In Lagowski, J.J., Ed., The Chemistry of Non-aqueous Solvents, Academic Press, New York and London, 1966, Vol 1, Chapter 4.
5. Parker, A.J. Chem. Rev. 69 (1969) 1, and earlier references quoted therein.
6. Alexander, R., Parker, A.J., Sharp, J.H. and Waghorne, W.E. J. Am. Chem. Soc. 94 (1972) 1148.
7. Kolthoff, I.M. and Chantooni, M.K. Jr. J. Phys. Chem. 76 (1972) 2024.
8. Popovych, O., Gibofsky, A. and Berne, D.H. Anal. Chem. 44 (1972) 811.
9. Cox, B.G. and Parker, A.J. J. Am. Chem. Soc. 95 (1973) 402.
10. Ahrland, S., Kullberg, L. and Portanova R. Acta Chem. Scand A 32 (1978) 251.
11. Cox, B.G., Hedwig, G.R., Parker, A.J. and Watts, D.W. Austr. J. Chem. 27 (1974) 477.
12. Ahrland, S. Pure Appl. Chem. 51 (1979) 2019.
13. Hedwig, G.R., Owensby, D.A. and Parker, A.J. J. Am. Chem. Soc. 97 (1975) 3888.
14. Ahrland, S. and Björk, N.-O. Acta Chem. Scand. A 28 (1974) 823.
15. Sandström, M., Persson, I. and Ahrland, S. Acta Chem. Scand. A 32 (1978) 607.

16. Potts, R.A. and Allred, A.L. Inorg. Chem. 5 (1966) 1066.
17. Rao, G.J. and Rao, K.B. Z. Anal. Chem. 168 (1959) 81.
18. Persson, H. Acta Chem. Scand. 24 (1970) 3739.
19. Parks, W.G. and LaMer, V.K. J. Am. Chem. Soc. 56 (1934) 90.
20. Clayton, W.J. and Vosburgh, W.C. J. Am. Chem. Soc. 58
(1936) 2093.
21. Schwarzenbach, G. and Flaschka, H. Die komplexometrische Titration, Enke, Stuttgart 1965, p. 214.
22. Handbook of Chemistry and Physics, 58th ed., CRC Press,
West Palm Beach 1977-1978, D-141.
23. Samojlenko, V.M., Lyashenko, V.I. and Polishchuck, N.V.
Russ. J. Inorg. Chem. 19 (1974) 1632.
24. Hietanen, S. and Sillén, L.G. Arkiv Kemi 10 (1956) 103.
25. Foll, A. Le Demezot, M. and Courtot-Coupez, J. Bull. Soc. Chim Fr. (1972) 1207.

Table 1. Standard electrode potentials in DMSO and water referred to $\underline{E}^{\circ}(\text{aq}) = 0$ for the silver electrode.

$\underline{I}/\underline{M} \rightarrow$	$\underline{E}^{\circ}(\text{DMSO})$		$\underline{E}^{\circ}(\text{aq})$
	1	0.15(0.1)	0
$\text{Ag}(\text{s})/\text{Ag}^{+}$	-349	-349	0
$\text{Cu}(\text{s})/\text{Cu}^{+}$	-686	-714	-277
$\text{Cu}(\text{s})/\text{Cu}^{2+}$	-710	-720	-459
$\text{Cu}^{+}/\text{Cu}^{2+}$	-734	-725	-641
$\text{Zn}(\text{s})/\text{Zn}^{2+}$	-1806	-1811	-1562
$\text{Cd}(\text{s})/\text{Cd}^{2+}$	-1492	-1498	-1202
$\text{Hg}(\text{l})/\text{Hg}^{2+}$	-301	-305	51
$\text{Hg}(\text{l})/\text{Hg}_2^{2+}$	-342	-350	-4
$\text{Hg}_2^{2+}/\text{Hg}^{2+}$	-261	-260	106

Table 2. Standard free energy, enthalpy and entropy changes of transfer from water to DMSO at 25°C ($\underline{\Delta G}_{tr}^{\circ}$, $\underline{\Delta H}_{tr}^{\circ}$ /kJ mol⁻¹; $\underline{\Delta S}_{tr}^{\circ}$ /JK⁻¹ mol⁻¹).

M^{nl}	$-\underline{\Delta G}_{tr}^{\circ}$	$-\underline{\Delta H}_{tr}^{\circ}$	$\underline{\Delta S}_{tr}^{\circ}$
Ag ⁺	34 ^a	55 ^b	-72
Cu ⁺	40		
Cu ²⁺	48		
Zn ²⁺	47	60 ^c	-44
Cd ²⁺	56	67 ^c	-37
Hg ²⁺	68	75 ^c	-26
Hg ₂ ²⁺	65		

^a Refs. 7,11 ^b Refs. 11,13 ^c Ref. 10

Table 3. Equilibrium constants, K_{ex} , and thermodynamic functions ($\Delta G_{\text{ex}}^{\circ}$, $\Delta H_{\text{ex}}^{\circ}/\text{kJ mol}^{-1}$; $\Delta S_{\text{ex}}^{\circ}/\text{JK}^{-1} \text{ mol}^{-1}$) for the reactions $M^{n+}(\text{DMSO}, \underline{I}=1) + n \text{Ag}^+(\text{aq}) = M^{n+}(\text{aq}) + n \text{Ag}^+(\text{DMSO}, \underline{I}=1)$, at 25°C .

M^{n+}	K_{ex}	$-\Delta G_{\text{ex}}^{\circ}$	$-\Delta H_{\text{ex}}^{\circ}$	$\Delta S_{\text{ex}}^{\circ}$
Cu^+	0.096	-5.8		
Cu^{2+}	2130	19.0		
Zn^{2+}	3750	20.4	50	-99
Cd^{2+}	99	11.4	43	-106
Hg^{2+}	0.75	-0.7	34	-116
Hg_2^{2+}	2.3	2.1		

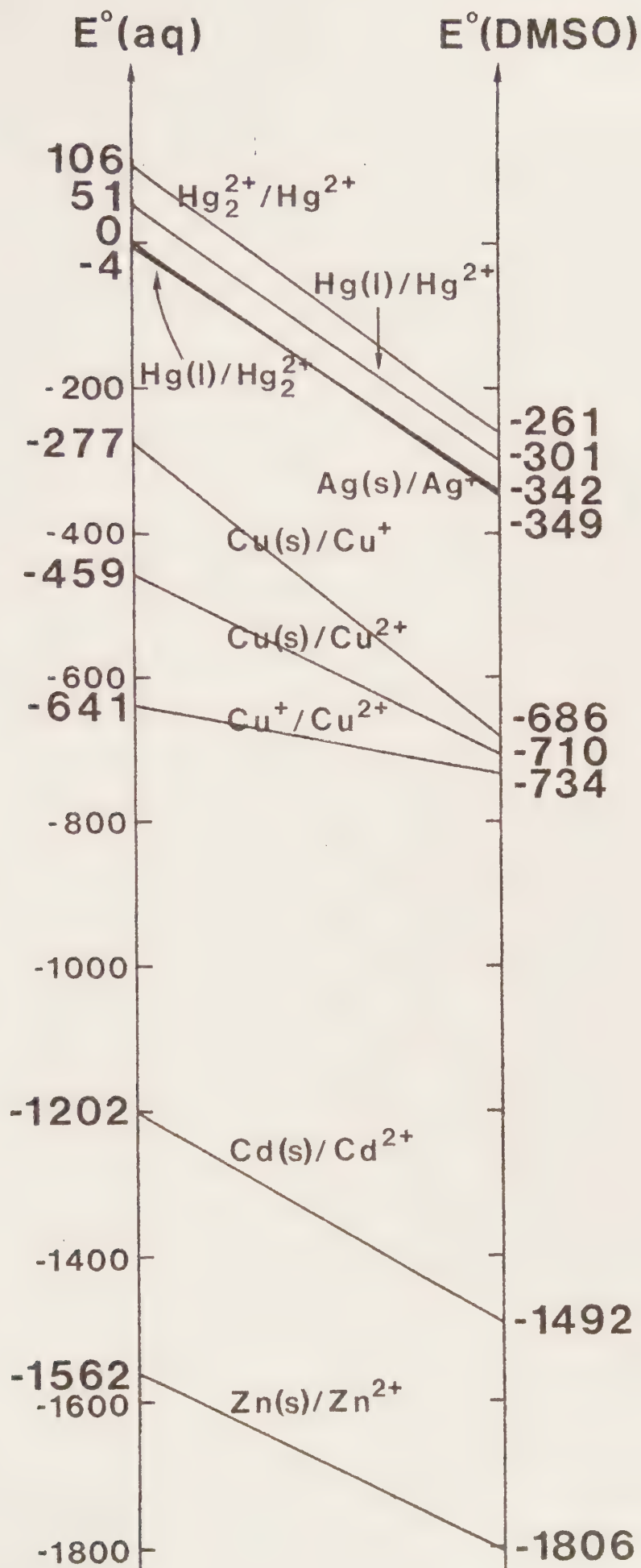
Table 4. The reproportionation constant $K_R = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$ in various DMSO and aqueous media, at 25°C, measured potentiometrically (E°) or by analysis of equilibrium solutions, attained from pure mercury(I) solvate (Hg(I)) or from pure mercury(II) solutions (Hg(II) + Hg(l)). Results from the present measurements, if not otherwise stated.

DMSO	NH_4ClO_4		Et_4NClO_4	NaClO_4^a	
I/M→	1	0.15	0.15	1	
E°	24.0±2.0	33.0±2.0		40±3	
Hg(I)	25.0±2.0	37 ±5			
Hg(II)+Hg(l)	24.5±2.0	36 ±5	40±5		
Mean	24.5±1.5	34.5±2.0			

Water ^b	NaClO_4		NaNO_3		
I/M→	1	0.15	1	0.15	0
E°	172	101	105	89	88±4

^a Ref. 23 ^b Ref. 24

Fig. 1. Standard electrode potentials in aqueous and dimethylsulfoxide solution, referred to $\underline{E}^0(\text{aq}) = 0$ for the $\text{Ag(s)}/\text{Ag}^+$ electrode.



Correspondence and proofs should be sent to

FK Ingmar Persson, Oorganisk kemi 1, Kemicentrum, Box 740,

S-220 07 Lund 7.

Running titles: Ahrland, Persson and Portanova

Metal Complexes in DMSO IX

Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide Solution. IX.

Equilibrium and Enthalpy Measurements on the Mercury(II) Chloride,

Bromide, Iodide and Thiocyanate Systems

STEN AHRLAND^a, INGMAR PERSSON^a and ROBERTO PORTANOVA^b

^a Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.

Box 740, S-220 07 Lund 7,

^b Istituto di Impianti Nucleari, Universita di

Palermo, Viale delle Scienze, I-901 28 Palermo, Italy

The thermodynamics of the formation of mercury(II) halide and thiocyanate complexes in dimethylsulfoxide (DMSO) has been investigated. The order of stability between the halide complexes follows a (b)-sequence, $\text{Cl}^- < \text{Br}^- < \text{I}^-$ though much less marked than in water. The levelling between the protic water and the aprotic DMSO is due to characteristic changes in both the enthalpy and the entropy contributions to the overall stabilities. In water, the values of both ΔH_j^0 , and of ΔS_j^0 , differ considerably between the systems; in DMSO these differences are largely smoothed out. As to ΔH_j^0 ,

a marked levelling also takes place between the consecutive steps of each system while the contrary is true for ΔS_j^0 . Especially the values of ΔS_1^0 are very large in DMSO. The thiocyanate ion behaves in many respects as the iodide ion but also has several traits of its own.

In water, hydrogen bonds are responsible both for an ordered solvent structure and a preferential solvation of ligands prone to hydrogen bonding, such as Cl^- . In DMSO, where no hydrogen bonds can be formed, these possibilities do not exist. The differences found between the two solvents for the systems investigated have been rationalized on this basis.

The complex formation of the divalent d^{10} acceptors Zn^{2+} , Cd^{2+} and Hg^{2+} with halide and thiocyanate ions reflect very different acceptor properties. In water, the halide complexes of Hg^{2+} are very stable and their stabilities moreover follow a very marked (b)-sequence: $\text{Cl}^- < \text{Br}^- < \text{I}^-$ ¹⁻³. With Cd^{2+} , much less stable complexes are formed, and the (b)-sequence is also much less marked^{3,4}. With Zn^{2+} , only very weak complexes are formed, and their stabilities moreover follow an (a)-sequence: $\text{Cl}^- > \text{Br}^- > \text{I}^-$ ^{3,5}.

In the aprotic solvent dimethylsulfoxide, (DMSO), the (a)-sequence of the Zn^{2+} complexes becomes much more marked⁶, while the mild (b)-sequence of the Cd^{2+} complexes turns into an (a)-sequence⁷. The complexes also become more stable than in water. These stability changes between the protic water and the aprotic DMSO are no doubt brought about mainly by two factors: the changes of the solvation of the ligands between the two solvents, and the less ordered structure of DMSO relative to water⁷⁻⁹. The former factor is the main cause of the change in the relative stabilities of the halide complexes. The latter is the main cause of the general increase of the

stabilities. Both effects are in the end due to the hydrogen bonding properties of the water molecules, a mode of bonding which has no counterpart in the aprotic DMSO. The conclusions drawn from the halide complex formation are further strengthened by the behaviour of the thiocyanate ion. For this ligand, the changes in the stabilities of the complexes between water and DMSO are reminiscent of those found for the iodide ion^{8,9}. This is to be expected, as both ligands have little capacity for hydrogen bonding.

These conclusions can only be reached if all the thermodynamic functions ΔG_j° and ΔS_j° of the consecutive complex formation reactions are known. For each system, not only the stabilities but also the heats of reaction have been measured. The stepwise stability constants K_j yield the free energy changes ΔG_j° , and by combining these with the enthalpy changes ΔH_j° the entropy changes ΔS_j° are finally found.

For Hg^{2+} , no complete investigation of the halide and thiocyanate complex formation has so far been done. The existing data indicate, however, that the (b)-sequence persists in DMSO, though much less marked than in water¹⁰⁻¹². From calorimetric data referring to the two later steps in the bromide and iodide systems it is also clear that an extensive levelling occurs between the values of ΔH_j° of the different halides¹³.

In the present study, all the thermodynamic functions pertaining to the Hg^{2+} complexes have been determined under the same conditions as used before for the Zn^{2+} and Cd^{2+} complexes, viz. in 1M ammonium perchlorate, at 25°C. This ionic medium allows a potentiometric determination of the stability constants by means of the mercury electrode while this electrode is attacked in waterfree lithium, sodium and tetraethylammonium perchlorate media¹⁴. The heats of reaction have been determined in separate calorimetric measurements.

EXPERIMENTAL

Chemicals. The source of Hg^{2+} was the solid $\text{Hg}(\text{ClO}_4)_2 \cdot 4 \text{ DMSO}$, prepared and analyzed as described previously¹⁵. The dimethylsulfoxide was first purified, stored and analyzed as before¹⁶. In the later experiments a volatile impurity still present was removed by a stream of dry nitrogen gas before the solvent was used. The mercury(II) perchlorate solutions were always prepared immediately before use, as their concentration decreases with time. For a 10 mM solution a decrease of 1% was found after 48 h, independent of whether the solutions had been stored in darkness or in diffuse daylight. Double distilled mercury was used without further purification. The cadmium amalgam contained 6,5% Cd, and was prepared and stored as described previously¹⁷. Other solutions were prepared as described previously¹⁶.

Potentiometric measurements. Metallic mercury reduces the solvated mercury(II) ion according to $\text{Hg(l)} + \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+}$. In the present DMSO medium¹⁸, the reproporationation constant $K_R = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}] = 24.5 \pm 2.0$. This value is considerably smaller than in aqueous media^{19,20}, but also in DMSO Hg_2^{2+} evidently predominates strongly over Hg^{2+} at equilibrium in solutions of the pure solvates. The mercury electrode can therefore only be used in the presence of ligands that prefer mercury(II) to mercury(I) so markedly that the divalent state is sufficiently stabilized. Fortunately, this is the case in the systems investigated here, where no appreciable reproporationation is found for ligand numbers $\bar{n} \gtrsim 1.5$. This implies that all the constants K_j can be determined.

To ensure that no solutions containing mercury(I) were included in the calculations, the mercury electrode compartment initially contained a ligand solution of a concentration, C_L' , high enough to bring about a value of $\bar{n}$

close to the upper limit of 4. In most cases, the solution initially also contained mercury(II), of the concentration $\underline{C}'_M = 10$ or 20 mM, corresponding to values of $\underline{C}'_L = 60$ and 100 mM, respectively. To this solution, aliquots of a solution of the same mercury(II) concentration $\underline{C}'_M$, but containing no ligand, was added. During the titration, the mercury(II), concentration thus stayed constant = $\underline{C}'_M$ while the ligand concentration, and hence $\bar{n}$, decreased. In some series, however, the initial ligand solutions, of $\underline{C}'_L = 15, 35$ or 70 mM, contained no mercury(II). During the titration with solutions of $\underline{C}'_M = 5, 10$ and 20 mM, respectively, the mercury concentration therefore increased while the concentration of ligand decreased. This procedure implies a more rapid decrease of the free ligand concentration $[L]$, and hence of $\bar{n}$. A cadmium amalgam electrode, with a cadmium(II) concentration of 20 mM and working in the same medium as the mercury electrode, was used as a reference. The emfs measured attained their final values within ≈ 20 min. They were generally reproducible within 0.3 mV and stayed constant within 0.5 mV for at least 15 hours.

To exclude moisture, the titrations were performed in dry atmosphere in a glove box. In addition, dry nitrogen saturated with DMSO was bubbled through the solutions during the measurements.

The emfs of the cells are given by $\underline{E} = \underline{E}^0 + (RT/2F)\ln[Hg^{2+}]$ where $\underline{E}^0$ is the potential of a standard mercury half-cell, $Hg(l)/Hg^{2+}$ relative to the cadmium reference cell used here. To relate the emfs measured with the concentrations $[Hg^{2+}]$ it is necessary to know $\underline{E}^0$. On account of the reproporationation reaction, this quantity cannot be directly measured but can be found from measurements of the $Hg(l)/Hg_2^{2+}$ and Hg_2^{2+}/Hg^{2+} couples. Under the present conditions, $\underline{E}^0 = 1190.65 \text{ mV}^{18}$.

The numerical calculations were performed by means of the computer program EMK^{21a}. The program had to be slightly modified, however, as the emfs $\underline{E} - \underline{E}^0$

of the present measurements always refer to galvanic cells with one hypothetical half-cell containing 1 M $[\text{Hg}^{2+}]$ while in the previous measurements the input values E_M referred to differences that were actually measured in each series.

Calorimetric measurements. The calorimeter and the procedure of measurements has been described previously^{7,22,23}. The calibration constant ε_V was redetermined and found to depend upon the total volume, V ml, according to $\varepsilon_V = a + b(V - 80)$, where $a = 0.9501 \pm 0.0025 \text{ J}^{-1}$ and $b = 1.3361 \pm 0.0028 \text{ J}^{-1}\text{ml}^{-1}$. For the halide systems, gold could still be used as material for calorimeter parts (inner vessel, etc) in contact with mercury(II) complex solutions, but this was not possible for the thiocyanate system. In the presence of this ligand, metallic gold is very rapidly oxidized by mercury(II), as is evident from the almost instantaneous formation of gold amalgam. Most probably, the formation of very strong gold(I) thiocyanate complexes brings down the oxidation potential of gold in DMSO to such a low value that the oxidation of mercury(II) becomes feasible, in spite of the fact that also mercury(II) is considerably stabilized by thiocyanate complex formation. An analogous reaction is brought about by triphenylphosphine in DMSO²⁴. In this case, rhodium coating of the gold parts has been found to prevent the reduction of mercury(II). Also the thiocyanate system could be measured in this modified calorimeter. One reason why rhodium is not at all attacked might be that this metal, contrary to gold, does not form an amalgam.

For each halide system, twelve titration series were performed. In six of these the calorimeter vessel initially contained mercury(II) perchlorate solutions and in the other ones solutions of the dihalide complex HgX_2 . With thiocyanate, seven titrations were performed, all starting with perchlorate

solutions in the calorimeter. The initial solutions, of 80 ml volume, had mercury(II) concentrations C'_M ranging from 4.0 to 16.0 mM. To these solutions, aliquots of ligand solution, of $C'_L = 100$ mM, were added, until a total solution volume of 100 ml. A volume of 20 ml was then withdrawn, and another titration with 20 ml ligand solution then performed. The procedure was repeated until a value of $\bar{n}$ close to 4 had been reached. Heats of dilution were measured not only for Hg^{2+} , but also for the complexes HgX^+ , HgX_2 and HgX_3^- . Such measurements are feasible in the present systems where each complex HgX_j^{2-j} predominates completely when $\bar{n} = j$. The heats were determined by titrating 16 mM solutions of each species with 1 M ammonium perchlorate. For Hg^{2+} , the heat of dilution was exothermic and relatively large, 0.08 J per ml solution added. For the complexes, the effects were quite small. The heats of dilution of the ligands were determined analogously⁷.

From the calorimetric data, the enthalpy changes have been calculated by the least squares program KALORI^{21b}, with the values of β_j found in the potentiometric measurements as fixed parameters. In all the systems investigated, the complexes formed are too stable to allow an independent determination of β_j from the calorimetric data²⁵.

Warning. Great caution must be exercised when handling DMSO solutions of mercury(II), mainly because of the skin-penetrating properties of the solutions^{26,27};

RESULTS

For all the halide systems, the potentiometric titrations show extended regions of low buffer capacity around the molar ratios 3 and 2 of ligand to mercury(II). This indicates that each consecutive complex HgX_j^{2-j} loses

one ligand almost completely before a further ligand starts to dissociate from the complex formed. Consequently, each complex predominates in the solutions over a fairly wide range of $[X^-]$, characterized by a practically constant ligand number $\bar{n} \approx j$. As already mentioned, this circumstance allows the separate determination of the heat of dilution for each species. Moreover, the amount of ligand added between the equivalence points provides a check of the concentration of mercury(II) present. The values of C'_M found in this way were throughout somewhat lower than those calculated from the analysis of the solid solvate used. As the difference was independent of C'_M , it could hardly be due to a reproportionation involving the formation of complexes of mercury(I). This conclusion was confirmed beyond doubt by the calorimetric measurements, where no reproportionation is possible. The values of ΔH_j^0 of the consecutive steps are different enough to produce fairly well-defined equivalence points. The values of C'_M calculated from these agree with the ones found potentiometrically. Most likely, the discrepancy is due to an impurity in the DMSO, with a strong affinity for mercury. The presence of dimethylsulfide might be suspected. As this compound is quite volatile (bp 37.3°C), it should be largely removed by a stream of nitrogen passing through the solvent. In the later series of measurements, this expedient was successfully tried. While the discrepancies amounted to 0.3 or 0.4 mM when ordinary DMSO was used, they were suppressed to at most 0.1 mM when the DMSO had been treated with nitrogen for 1 hr. The values determined by the equivalence points were always ^{used} in the calculations which gave consistent results.

In the thiocyanate system, the concentration of the complex $Hg(SCN)_3^-$ never exceeds $\approx 50\%$ of the total mercury(II) concentration. Consequently, no equivalence point develops at $\bar{n} = 3$. The value of C'_M to be used cannot

therefore, be determined directly from the potentiometric measurements. The calorimetric measurements provide, however, a precise value of the correction, viz. 0.4 mM, from the well-defined equivalence point $\bar{n} = 2$. With this correction applied, also the potentiometric data yield a consistent result.

For all the systems, the potentiometric data can be interpreted by the formation of the four mononuclear complexes HgX_j^{2-j} , $j = 1 - 4$, provided that the value of $\bar{n} > 1.45$. The emfs measured below this limit become increasingly ill-fitted to this scheme as the value of $\bar{n}$ decreases which evidently reflects the growing reproportionation.

The overall stability constants calculated are listed, with their limits of error, in Table 1. The complex formation functions found from these constants are presented in the upper part of Fig. 1. The predominance of each consecutive complex HgX_j^{2-j} (with the sole exception of $\text{Hg}(\text{SCN})_3^-$) at the value of $\bar{n} = j$ is immediately evident. The conditions are even more strikingly illustrated by the distribution curves presented in Fig. 2. The maximum share of the total mercury(II) concentration (attained at $\bar{n} = j$) is for most of the complexes well over 90%. The third complex is throughout the least stable relative to its neighbours; as already pointed out, this applies especially to $\text{Hg}(\text{SCN})_3^-$.

The quantity directly obtained from the calorimetric measurements, viz. the heat evolved per mole mercury(II), Δh_v is plotted as a function of $\bar{n}$ for the various systems in Figs. 3 and 4. All the complexes are evidently formed in exothermic reactions. As already mentioned, the differences between the values of ΔH_j^0 for two consecutive steps are in most instances so large that marked deflections occur at the equivalence points. The values of the overall enthalpy changes $\Delta H_{\beta j}^0$ calculated from the values of Δh_v are listed, with their limits of error, in Table 2.

In the Tables 1 and 2, the number of observations performed for each system (NP) is also reported.

DISCUSSION

Quantities related to the consecutive steps. From the values of β_j obtained, the stepwise stability constants K_j and the standard free energy changes ΔG_j° are calculated for each consecutive step. From the values of $\Delta H_{\beta_j}^\circ$, the stepwise enthalpy changes ΔH_j° are calculated, and by combining these with ΔG_j° the stepwise entropy changes ΔS_j° are obtained. In Table 3, the values found are compared with those previously determined for the same systems in aqueous solutions. Here, the most representative results refer to sodium perchlorate media but such a change of medium certainly means little compared to the change of solvent³. This is also confirmed by the stability constants found for the present systems in DMSO solutions containing various supporting electrolytes, Table 4. The ratios K_j / K_{j+1} have also been entered for both solvents.

Stability constants, and their ratios. Also in DMSO, the stabilities of the halide complexes follow a (b)-sequence, though much less marked than in water. The present study thus definitely confirms the main result of the previous investigations¹⁰⁻¹². As these moreover refer to other media, viz. 0.1 M Et_4NClO_4 and 1 M NaClO_4 or LiClO_4 , it is evident that the influence of the medium is indeed small compared to that of the solvent. Also measurements of the mercury(II) bromide system performed in 0.1 M NH_4ClO_4 support this conclusion²⁸, Table 4.

Though the main picture is not changed, marked differences nevertheless exist between 1 M NH_4ClO_4 on one hand, and the other media on the other. These are quite substantial for chloride, smaller for bromide and very small

for iodide. They are certainly due to hydrogen bond formation between NH_4^+ and the halide ions, strongly decreasing in strength in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ ²⁸. At high values of $[\text{NH}_4^+]$ this complex formation evidently involves a strong competition for ligands of marked hydrogen bonding properties.

The levelling implies large increases in the overall stabilities of the chloride complexes, and sizable ones in the stabilities of the bromide complexes, while the stabilities of the iodide complexes change very little. The changes are very different for the consecutive steps, however. Especially the first and third steps are favoured in DMSO relative to water. The second step, on the other hand, shows only a modest increase of stability even in the chloride system and a decrease in the bromide and, especially, in the iodide system. The thiocyanate complexes behave much like the iodide ones, though they are, on the whole, even less favoured by the transfer to DMSO. Especially the strong suppression of the second complex should be noted.

The changes of the relative stabilities of the consecutive complexes taking place on the transfer from water to DMSO are reflected in large changes of the ratios $\underline{K}_j / \underline{K}_{j+1}$, Table 3. In water, the ratios $\underline{K}_2 / \underline{K}_3$ are very large, as is shown by the very extended horizontal portions of the complex formation curves found at $\bar{n} = 2$, cf. lower part of Fig. 1. These ratios are much smaller in DMSO, but still large enough to bring about marked plateaus at $\bar{n} = 2$, cf. upper part of Fig. 1. The ratios $\underline{K}_1 / \underline{K}_2$ and $\underline{K}_3 / \underline{K}_4$ are generally quite small in water, and therefore no inflexions develop at $\bar{n} = 1$ and 3, except for a very slight one at $\bar{n} = 1$ in the iodide curve, Fig. 1. In DMSO, on the other hand, the ratios are large enough to bring about marked plateaus, except at $\bar{n} = 3$ in the thiocyanate curve. The relative changes of stability between water and DMSO thus result:

in that predominance of each complex (except $\text{Hg}(\text{SCN})_3^-$) within a certain range of $[\text{L}]$ which is such a striking feature of the complex formation in the latter solvent, Figs. 1 and 2.

Enthalpy changes. The levelling of the stabilities is brought about by a very considerable levelling of the values of ΔH_j^0 between water and DMSO, Table 3. Especially for the first two steps, the effect is very large. While the differences in water between the chloride and iodide systems are 50.6 for ΔH_1^0 and 38.9 kJ mol^{-1} for ΔH_2^0 , respectively, they are only 12.9 and 10.6 kJ mol^{-1} in DMSO. Analogous decreases, though smaller, are found between chloride and bromide. As already mentioned, this levelling must mainly be due to the relative change of solvation of the ligands. While Cl^- , prone to hydrogen bonding, is more strongly solvated in the protic water than in the aprotic DMSO, the contrary is true for I^- , of little hydrogen bonding capacity. This is reflected in the transfer enthalpies between water and DMSO, $\Delta H_{\text{tr}}^0 (\text{W} \rightarrow \text{DMSO})$, which for these ions are 18.8 and -12.8 kJ mol^{-1} , respectively^{9,29}. Consequently, the difference $- [\Delta H_{\text{sv}}^0 (\text{Cl}^-) - \Delta H_{\text{sv}}^0 (\text{I}^-)]$ between the solvation enthalpies is 31.6 kJ mol^{-1} smaller in DMSO than in water. This implies per se a decrease by this amount of the differences between the values of ΔH_j^0 on a transfer of the chloride and iodide systems from water to DMSO. In the case of Br^- $\Delta H_{\text{tr}}^0 (\text{W} \rightarrow \text{DMSO}) = 3.5 \text{ kJ mol}^{-1}$ which definitely indicates a capacity for hydrogen bonding in water²⁹. This is also in compliance with the behaviour of the bromide complexes on their transfer from water to DMSO.

Especially for I^- , but also for Br^- , the values of $-\Delta H_1^0$ decrease very much from water to DMSO, Table 3. This must mainly be due to the stronger solvation of Hg^{2+} in DMSO³⁰, reflected in the large value of $\Delta H_{\text{tr}}^0 (\text{W} \rightarrow \text{DMSO})$ -76 kJ mol^{-1} . For I^- , the effect is further enhanced by the higher value

of $-\Delta H_{sv}^0(I^-)$. That the total effect does not amount to more than 42.1 and 17.5 kJ mol⁻¹ for I⁻ and Br⁻, respectively, must largely be due to the circumstance that also the values of $-\Delta H_{sv}^0(HgX^+)$ are certainly higher in DMSO than in water. Moreover, the lower value of the dielectric constant in DMSO, $\epsilon = 46.4^{26}$, must contribute to more exothermic values of ΔH_1^0 , by increasing the electrostatic interaction between Hg²⁺ and X⁻. In the case of Cl⁻, the changes between water and DMSO in the terms contributing to ΔH_1^0 almost compensate each other. The values of ΔH_2^0 show similar trends, though less marked, Table 3. For I⁻ and Br⁻, the second step is still much less exothermic in DMSO than in water, and the reasons must be analogous to these advanced for the first step.

In contrast to ΔH_1^0 and ΔH_2^0 , the values of ΔH_3^0 and ΔH_4^0 are generally more exothermic in DMSO than in water. This applies especially to the chloride system. The reason for this difference between the earlier and later steps is certainly that the desolvation has gone very far with the formation of the second complex. In the following steps, the desolvation enthalpies should therefore not be very important and hence not able to bring about a decrease of $-\Delta H_3^0$ or $-\Delta H_4^0$ when the systems are transferred from water to DMSO. This interpretation also agrees with the magnitude of the entropy changes of the various steps, as will be further discussed below.

That the desolvation is indeed very extensive after the first two steps has been shown by independent thermodynamic measurements. Thus, the solvation enthalpies $\Delta H_{sv}^0(HgX_2)$ of the neutral complexes are only $\approx 5\%$ of $\Delta H_{sv}^0(Hg^{2+})^{30}$. Even more significant, they are less than half of the solvation enthalpies of the formally analogous complexes CdX₂ and ZnX₂, in spite of the fact that $\Delta H_{sv}^0(Hg^{2+})$, $\Delta H_{sv}^0(Cd^{2+})$ and $\Delta H_{sv}^0(Zn^{2+})$ are all of the same order of magnitude³⁰.

A direct proof of this desolvation has further been provided by structure

determinations of the species present in the solutions, performed by means of X-ray diffraction studies. In solution, Hg^{2+} coordinates octahedrally six DMSO (by their oxygens) at the close distance $2.39 \text{ \AA}^{15}$ (which is close to the distance found in the corresponding solid solvate³¹, $2.34 \text{ \AA}$). In the complexes HgX_2 , only the distances Hg to S can be discerned. These are $\approx 0.2 \text{ \AA}$ longer than in $\text{Hg}(\text{DMSO})_6^{2+}$, corresponding to Hg - O distances $\approx 2.6 \text{ \AA}^{32}$. The considerable lengthening means a much weaker bond. The number of Hg - O bonds in the complexes HgX_2 is difficult to ascertain, but is in any case not higher than four which of course also contributes to a weaker overall solvation.

A previous calorimetric determination¹³ of $\underline{\Delta H}_3^0$ and $\underline{\Delta H}_4^0$ for the bromide and iodide systems in 1 M NaClO_4 agrees quite well with the present results, Table 5. Also the values of $\underline{K}_3$ and $\underline{K}_4$ calculated from these measurements are in fair agreement with those found potentiometrically in the present study. On account of the low solubility of NaCl in DMSO³³, the chloride system could not be investigated.

In other calorimetric investigations^{34,35}, the formation of the complex ML_j has been assumed to be complete when $\underline{C}_L / \underline{C}_M = j$ (i.e. $[\text{L}] \approx 0$ over the whole range of complex formation). As this is certainly not the case in the last step, the values of $-\underline{\Delta H}_4^0$ calculated are much too low, Table 5. Also the values of $-\underline{\Delta H}_3^0$ differ considerably from those found in the other investigations, however, Tables 3 and 5.

The changes of $\underline{\Delta H}_j^0$ taking place between the two solvents imply that the pattern which is so characteristic for aqueous solutions, with $-\underline{\Delta H}_1^0$ and $-\underline{\Delta H}_2^0$ large and of about the same size, and with $-\underline{\Delta H}_3^0$ and $-\underline{\Delta H}_4^0$ much smaller, is largely smoothed out in DMSO, Table 3. In this solvent, the change of structure³² taking place between the digonal HgX_2 and the trigonal, or pyramidal, HgX_3^- is therefore not at all as clearly indicated by the $\underline{\Delta H}_j^0$

values as it is in water.

A characteristic feature of all the systems in DMSO is, on the other hand, that $-\Delta H_2^0 > -\Delta H_1^0$. Evidently, the desolvation taking place in the first step is so extensive, and the desolvation enthalpy needed consequently so large, that the net enthalpy change becomes less exothermic than for the second step, in spite of the fact that the heat evolved on the formation of the new Hg - X bond is certainly larger in the first step. The later conclusion rests on the observation that the length of the Hg - X bond generally increases with the number of ligands coordinated, indicating a corresponding decrease in the bond strength^{32,36,37}. This decrease should moreover be the main cause of the monotonous decrease of $-\Delta H_j^0$ found in DMSO between the later steps of all the halide systems, Table 3 and Fig. 5.

In the thiocyanate system, the values of $-\Delta H_1^0$ and $-\Delta H_2^0$ decrease between water and DMSO in much the same manner as in the halide systems, Table 3. The higher steps behave differently, however. Contrary to what is found for the halides, they become less exothermic in DMSO, and the pattern is moreover different, with $-\Delta H_4^0 > -\Delta H_3^0$. Seemingly, the structures of the complexes in solution are not wholly analogous to those formed in the halide systems, as is further indicated by the entropy changes discussed below.

For the overall reactions $\text{Hg}^{2+} + 4 \text{X}^- \rightleftharpoons \text{MX}_4^{2-}$, the changes between water and DMSO mean a large decrease of enthalpy stabilization for $\text{X}^- = \text{I}^-$ and SCN^- , a modest decrease for Br^- and a modest increase for Cl^- , cf. the values of $\Delta H_{\beta 4}^0$ in Table 3.

Entropy changes. Relative to water, the entropy terms are so favourable in the aprotic DMSO that the loss of stabilities due to the less exothermic values of $\underline{\Delta H}_1^0$ and $\underline{\Delta H}_2^0$ are more than compensated. The values of $\underline{\Delta S}_1^0$, are indeed huge in DMSO and also the values of $\underline{\Delta S}_2^0$ are quite considerable, Table 3. For both $\underline{\Delta S}_1^0$ and $\underline{\Delta S}_2^0$, the differences between water and DMSO grow from Cl^- to I^- . This results in a marked levelling the values of the different halides, just as has been found also in the case of $\underline{\Delta H}_1^0$ and $\underline{\Delta H}_2^0$.

The large increases of $\underline{\Delta S}_1^0$ and $\underline{\Delta S}_2^0$ relative to water are no doubt mainly due to the lower degree of order in DMSO. In water, the desolvation reactions imply that water molecules leave the hydrates for the bulk water which, however, has a fairly well-ordered structure brought about by intermolecular hydrogen bonds. Such a process involves at most a modest entropy gain. If the formation of the complex per se means a sufficiently large increase of the degree of order, as is the case for I^- , a net loss of entropy may even occur. In DMSO, on the other hand, solvent molecules leave the solvates for a fairly unstructured bulk solvent which results in a large entropy gain. A further increase is brought about by the circumstance that the DMSO solvates have to be more strictly ordered than the corresponding hydrates, in order to accomodate the more bulky and less symmetrical DMSO molecules in the preferred arrangements. This is very evident in the case of the hexasolvates^{15,31,39} $\text{Hg}(\text{DMSO})_6^{2+}$ and $\text{Hg}(\text{H}_2\text{O})_6^{2+}$ but presumably applies also to the solvates of the complexes, and the ligands.

The values of $\underline{\Delta S}_3^0$ and $\underline{\Delta S}_4^0$ are, on the other hand, fairly small in DMSO; $\underline{\Delta S}_3^0$ slightly positive, $\underline{\Delta S}_4^0$ slightly negative. This again indicates that the desolvation is much less important in the later steps and especially for the formation of MX_4^{2-} . This is also confirmed by the fact that the

values of $\underline{\Delta S}_3^0$ and $\underline{\Delta S}_4^0$ in DMSO are not drastically different from those found in water.

In water, the total entropy change $\underline{\Delta S}_{\beta 4}^0$ for the reaction $\text{Hg}^{2+} + 4 \text{X}^- \rightleftharpoons \text{HgX}_4^{2-}$ decreases fairly rapidly in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$, reflecting the strong decrease of solvation of these ligands in the same order. In DMSO, however, much the same values of $\underline{\Delta S}_{\beta 4}^0$ are found for all halides. The differences in solvation are much smaller in this solvent and what remains is evidently compensated by other entropy contributions.

For the thiocyanate complexes the entropy changes are throughout less favourable than for the halides complexes, Table 3. This is evidently due to the loss of conformational entropy accompanying the coordination of a ligand of much lower symmetry than the halide ions. The overall gain $\underline{\Delta S}_{\beta 4}^0$ is hardly larger than half the values found for the halides.

The values of $\underline{\Delta S}_j^0$ follow a pattern different from that of the halides, as was also found for the values of $\underline{\Delta H}_j^0$, Table 3. In the thiocyanate system $\underline{\Delta S}_3^0 > \underline{\Delta S}_2^0$, while a monotonous decrease of $\underline{\Delta S}_j^0$ takes place in the case of the halides. The solvation of the second complex is evidently relatively stronger in the thiocyanate system, presumably implying a structure appreciably different from that of the formally analogous halide complexes HgX_2 .

Contributions from enthalpy and entropy terms to the decrease of free energy. A general view of the relative importance of the enthalpy and entropy contributions to the stabilities of the complexes formed is provided by Fig. 5. The strong entropy stabilization of the first complex in all the systems is evident. For Cl^- , the entropy change contributes twice as much as the heat of reaction to the stability, and even for SCN^- , the two terms are of about the same size. For all the halides, the entropy

contribution is still important in the second step, providing about one third of the total decrease of free energy, but drops into insignificance in the following steps. These are therefore heavily enthalpy stabilized, in spite of the gradual decrease of ΔH_j^0 . In the case of SCN^- , however, the trend is reversed relative to the halides both between ΔS_2^0 and ΔS_3^0 , and between ΔH_3^0 and ΔH_4^0 . As a result, the third complex, but not the second one, is appreciably entropy stabilized in this system. Related differences between halide and thiocyanate complexes have also been found for cadmium(II), both in DMSO and water⁷. As already pointed out, they certainly reflect a difference in structure between formally analogous thiocyanate and halide complexes.

Acknowledgement. We gratefully acknowledge the generous support given to these investigations by "Naturvetenskapliga Forskningsrådet"

(The Swedish Natural Science Research Council). The calorimetric study of the thiocyanate system was performed with the modified instrument available at Chemistry Department -I (Inorganic Chemistry), H.C. Ørsted Institute, University of Copenhagen. Our thanks are due to the staff of this Department and particularly to licentiat Torsten Berg, for their help and hospitality.

REFERENCES

1. Ahrland, S., Chatt, J. and Davies, N.R. Quart. Rev. Chem. Soc. 12 (1958) 265.
2. Sillén, L. G. Acta Chem. Scand. 3 (1949) 539.
3. Sillén, L. G. and Martell, A.E., Eds., Stability Constants of Metal-Ion Complexes, Chemical Society, Special Publications Nos. 17 and 25, London 1964, 1971.
4. Gerding, P. Acta Chem. Scand. 20 (1966) 79.
5. Gerding, P. Acta Chem. Scand. 23 (1969) 1695.
6. Ahrland, S., Björk, N.O. and Portanova, R. Acta Chem. Scand. A 30 (1976) 270.
7. Ahrland, S. and Björk, N.O. Acta Chem. Scand. A 30 (1976) 257.
8. Ahrland, S. In Lagowski, J.J., Ed., The Chemistry of Nonaqueous Solvent, Academic Press, New York San Francisco London 1978, Vol. V A, Chapter 1.
9. Ahrland, S. Pure Appl. Chem. 51 (1979). In press.
10. Foll, A., Le Demez, M. and Courtot-Coupez, J. Bull. Chem. Soc. Fr. (1972) 1207.
11. Samoilenko, V.M., Lyashenko, V.I. and Polishchuk, N.V. Zh. Neorg. Khim. 19 (1974) 2984.
12. Balyatinskaya, L.N. Zh Neorg. Khim. 20 (1975) 3210.
13. Arnek, R. and Poceva, D. Acta Chem. Scand. A 30 (1976) 59.
14. Ahrland, S. and Persson, I. To be published.
15. Sandström, M., Persson, I. and Ahrland, S. Acta Chem. Scand. A 32 (1978) 607.

16. Åhrland, S. and Björk, N.O. Acta Chem. Scand. A 28 (1974) 823.
17. Persson, H. Acta Chem. Scand. 24 (1970) 3739.
18. Åhrland, S. and Persson, I. To be published.
19. Schwarzenbach, G. and Anderegg, G. Helv. Chim. Acta 37 (1954) 1289.
20. Hietanen, S. and Sillén, L.G. Arkiv Kemi 10 (1956) 103.
- 21.a Karlsson, R. and Kullberg, L. Personal communication.
- 21.b Karlsson, R. and Kullberg, L. Chem. Ser. 9 (1976) 54.
22. Grenthe, I, Ots, H, and Ginstrup, O. Acta Chem. Scand. 24 (1970) 1067.
23. Ots, H. Acta Chem. Scand. 26 (1972) 3810.
24. Åhrland, S., Berg, T. and Bläuenstein, P. Acta Chem. Scand. A 32 (1978) 933.
25. Christensen, J.J., Ruckman, J., Eatough, D.J. and Izatt, R.M. Thermochim. Acta 3 (1972) 203.
26. Reynolds, W.L. In Lippard, S.J., Ed., Progress in Inorganic Chemistry, Interscience, New York London Sydney Toronto 1970, Vol. 12, Chapter 1.
27. Martin, D. and Hauthal, H.G. Dimethyl Sulphoxide, van Nostrand Reinhold, Wokingham, Berkshire 1975, p. 448.
28. Åhrland, S. and Persson, I. To be published.
29. Krishnan, C.V. and Friedman, H.L. J. Phys. Chem. 73 (1969) 3934.
30. Åhrland, S., Kullberg, L. and Portanova, R. Acta Chem. Scand. A 32 (1978) 251.
31. Sandström, M. and Persson, I. Acta Chem. Scand. A 32 (1978) 95.
32. Sandström, M. Acta Chem. Scand. A 32 (1978) 627.
33. Kenttämää, J. Soum. Kemistilehti 33 B (1960) 179.

34. Gorenbein, E.Y., Vainshtein, M.N., Skorobogatko, E.P. and Trofinchuk, A.K. Zh. Obshch. Khim. 44 (1974) 1558.
35. Gorenbein, E.Y., Vainshtein, M.N. and Skorobogatko, E.P. Ukr. Khim. Zh. 9 (1974) 923.
36. Åhrland, S., Hansson, E., Iverfeldt, Å. and Persson, I. To be published.
37. Gaizer, F. and Johansson, G. Acta Chem. Scand. 22 (1968) 3013.
38. Johansson, G. and Sandström, M. Acta Chem. Scand. A 32 (1978) 109.
39. Marcus, Y., Acta Chem. Scand. 11 (1957) 599.
40. Gallagher, P.K. and King, E.L., J. Am. Chem. Soc. 82 (1960) 3510.
41. Björkman, M. and Sillén, L.G., Trans. Royal Inst. Technol. Stockholm (1963) No. 199.
42. Christensen, J.J., Izatt, R.M., Hansen, L.D. and Hale, J.D., Inorg. Chem. 3 (1964) 130.
43. Åhrland, S. and Kullberg, L., Acta Chem. Scand. 25 (1971) 3692

Table 1. Overall stability constants (β_j/M^{-j}) of the mercury(II) halide and thiocyanate complexes in DMSO, at 25°C. Medium 1 M NH_4ClO_4 . The limits of error refer to three standard deviations; NP denotes the number of observations (emfs measured) for each system.

Ligand	Cl^-	Br^-	I^-	SCN^-
β_1	$(7.41 \pm 0.53) \cdot 10^{10}$	$(1.38 \pm 0.16) \cdot 10^{12}$	$(3.31 \pm 0.29) \cdot 10^{13}$	$(2.14 \pm 0.17) \cdot 10^9$
β_2	$(9.26 \pm 0.77) \cdot 10^{17}$	$(1.57 \pm 0.21) \cdot 10^{20}$	$(1.88 \pm 0.13) \cdot 10^{23}$	$(9.85 \pm 1.05) \cdot 10^{14}$
β_3	$(9.13 \pm 1.03) \cdot 10^{21}$	$(2.16 \pm 0.40) \cdot 10^{25}$	$(1.92 \pm 0.14) \cdot 10^{29}$	$(8.93 \pm 1.31) \cdot 10^{17}$
β_4	$(1.09 \pm 0.24) \cdot 10^{24}$	$(7.42 \pm 2.16) \cdot 10^{27}$	$(8.12 \pm 0.49) \cdot 10^{31}$	$(1.84 \pm 0.51) \cdot 10^{20}$
NP	323	372	346	317

Table 2. Overall enthalpy changes ($\Delta H_{\beta j}^{\circ}/\text{kJ mol}^{-1}$) for the formation of the mercury(II) halide and thiocyanate complexes in DMSO, at 25°C. Medium 1 M NH_4ClO_4 . The limits of error refer to three standard deviations; NP denotes the number of observations (aliquots added) for each system.

Ligand	Cl^-	Br^-	I^-	SCN^-
$-\Delta H_{\beta 1}^{\circ}$	$20.3^{+0.8}$	$24.7^{+0.8}$	$33.2^{+0.8}$	$28.1^{+0.9}$
$-\Delta H_{\beta 2}^{\circ}$	$48.8^{+1.2}$	$56.6^{+1.2}$	$72.6^{+1.2}$	$59.1^{+1.3}$
$-\Delta H_{\beta 3}^{\circ}$	$68.9^{+1.4}$	$84.4^{+1.3}$	$100.7^{+1.4}$	$68.9^{+2.3}$
$-\Delta H_{\beta 4}^{\circ}$	$82.9^{+1.9}$	$103.5^{+1.6}$	$121.8^{+1.7}$	$85.6^{+2.6}$
NP	255	253	260	180

Table 3. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔC_j^0 , $\Delta H_j^0/kJ\ mol^{-1}$; $\Delta S_j^0/JK^{-1}\ mol^{-1}$) for the stepwise formation of mercury(II) halide and thiocyanate complexes in DMSO and water, at 25°C.

	DMSO				Water			
	1 M NH_4ClO_4				0.5 M $NaClO_4$			
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-
$\log K_1$	10.87	12.14	13.52	9.33	6.74	9.05	12.87	9.08
$\log K_2$	7.10	8.06	9.76	5.66	6.48	8.28	10.95	7.78
$\log K_3$	3.99	5.14	6.01	2.96	0.85	2.41	3.78	2.84
$\log K_4$	2.08	2.54	2.62	2.31	1.00	1.26	2.23	1.97
K_1/K_2	5930	12100	5810	4660	1.8	5.9	83	20
K_2/K_3	1270	830	5540	510	4×10^5	7×10^5	1.5×10^7	9×10^4
K_3/K_4	82	400	2450	4.4	0.7	14	35	7
$-\Delta G_1^0$	62.0	69.3	77.2	55.3	38.5	51.7	73.5	51.8
$-\Delta G_2^0$	40.5	46.0	55.7	32.2	37.0	47.3	62.5	44.4
$-\Delta G_3^0$	22.8	29.3	34.3	16.9	4.9	13.8	21.6	16.2
$-\Delta G_4^0$	11.9	14.5	15.0	13.2	5.7	7.2	12.7	11.2

$-\Delta H_1^{\circ}$	20.3	24.7	33.2	28.1	24.7	42.2	75.3	49.7
$-\Delta H_2^{\circ}$	28.5	31.9	39.4	31.1	28.9	44.8	67.8	50.4
$-\Delta H_3^{\circ}$	20.1	27.8	28.1	9.7	9.2	12.0		20.4
$-\Delta H_4^{\circ}$	14.0	19.1	21.1	16.8	0.4	17.2		21.0
ΔS_1°	140	149	148	85	46	32	-6	7
ΔS_2°	40	47	54	4	27	8	-18	-20
ΔS_3°	9	5	21	24	-14	6		-14
ΔS_4°	-7	-16	-21	-12	20	-33		-33
$-\Delta H_{\beta_4}^{\circ}$	82.9	103.5	121.8	85.6	62.4	116.2	185	141.5
$\Delta S_{\beta_4}^{\circ}$	182	186	202	100	79	13	-49	-60

^a This work. The values pertaining to the thiocyanate system differ slightly from a preliminary set published previously⁹ which had been calculated without correction for the impurity present in the solvent (cf. above).

^b Ref. 2, 39-42 ^c Ref. 43

Table 4. Previously determined stability constants (β_j/M^j) of mercury(II) halide and thiocyanate complexes in DMSO, at 25°C.

	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	Cl ⁻	Br ⁻	I ⁻	SCN ⁻
	0.1 M (C ₂ H ₅) ₄ NC1O ₄ ^a				1 M LiClO ₄ ^b 1 M NaClO ₄ ^b			
log β ₂	21.2	22.2	24.2	16.1	21.1			16.1
log β ₃	26.9	28	30.4	19.1	26.9	28.3	30.4	19.0
log β ₄		30.4	32.6	21.2	28.3	29.2	32.3	20.4
	Medium unknown ^c							
log β ₁	13.40	14.60	16.00	10.70	0.1 M NH ₄ ClO ₄ ^e			
	1 M NH ₄ ClO ₄ ^d							
log β ₁	10.87	12.14	13.52	9.33		12.92		
log β ₂	17.97	20.20	23.27	14.99		21.96		
log β ₃	21.96	25.33	29.28	17.95		27.62		
log β ₄	24.04	27.87	31.91	20.26		30.22		

^a Ref 10 ^b Ref 11 ^c Ref 12; presumably no supporting salt added. ^d This work ^e Ref 28

Table 5. Previously determined stepwise stability constants ($\underline{K}_j/M^{-1}$) and thermodynamic functions

($\underline{\Delta G}_j^\circ$, $\underline{\Delta H}_j^\circ/kJ\ mol^{-1}$; $\underline{\Delta S}_j^\circ/JK^{-1}\ mol^{-1}$) for the formation of mercury(II) halide and thiocyanate complexes in DMSO, at 25°C.

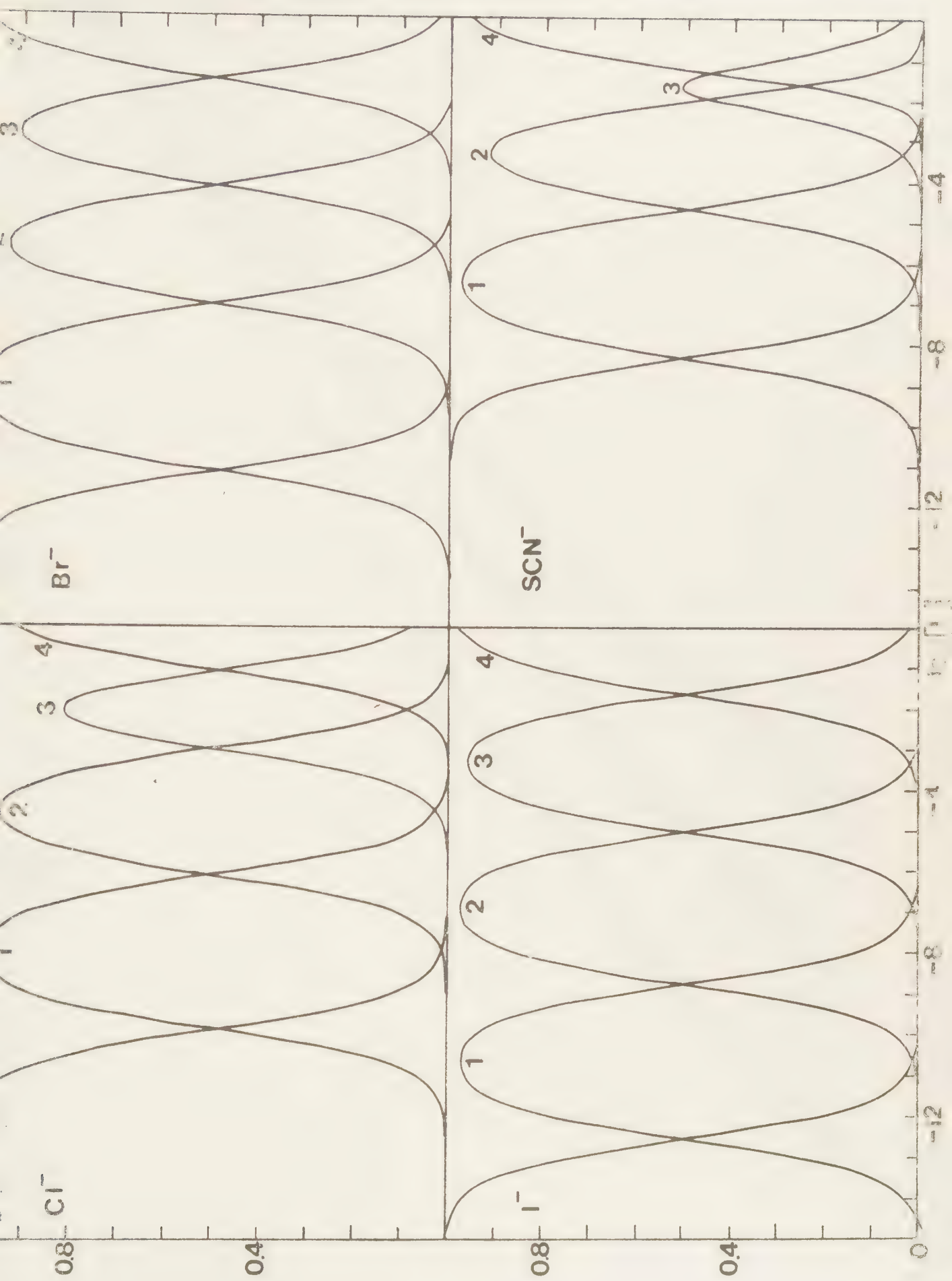
	1 M NaClO ₄ ^a		Li-medium ^b			Na-medium ^c	
	Br ⁻	I ⁻	Cl ⁻	Br ⁻	I ⁻	I ⁻	SCN ⁻
log $\underline{K}_3$	5.6	6.1					
log $\underline{K}_4$	2.65	2.55					
$\underline{K}_3/\underline{K}_4$	890	3310					
$-\underline{\Delta G}_3^\circ$	32.0	34.8					
$-\underline{\Delta G}_4^\circ$	15.1	14.7					
$-\underline{\Delta H}_3^\circ$	26.9	26.8	20.9	23.4	30.9	32.2	
$-\underline{\Delta H}_4^\circ$	22.7	22.8	13.4	13.8	11.3	11.3	15.4
$\underline{\Delta S}_3^\circ$	17	27					
$\underline{\Delta S}_4^\circ$	-25	-27					

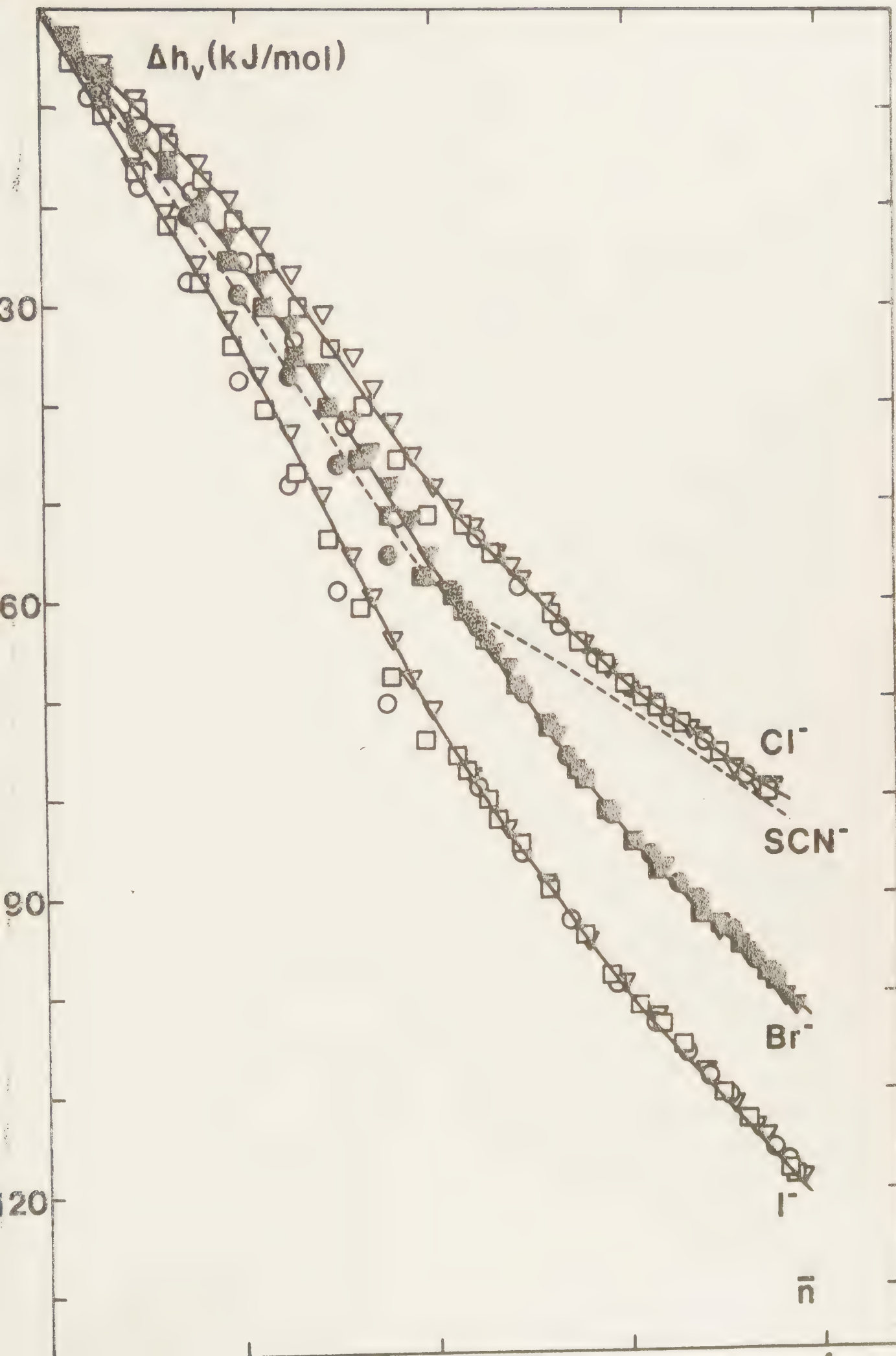
^a Ref 13; ^b Ref 34; ^c I⁻: ref 35; SCN⁻: ref 34

Legends to the Figures:

- Fig. 1. The complex formation curves of the mercury(II) halide and thiocyanate systems in DMSO and aqueous solutions, at 25°C. DMSO; fulldrawn curves: chloride (1), bromide (2) and iodide (3); dotted curve: thiocyanate; all in 1 M NH_4ClO_4 ; dashed curve: bromide in 0.1 M NH_4ClO_4 . Aq; fulldrawn curves: chloride (1), bromide (2) and iodide (3), in 0.5 M NaClO_4 ; dotted curve: thiocyanate, in 1 M NaClO_4 ; dashed curve: chloride, in 3 M NaClO_4 .
- Fig. 2. Distribution in DMSO of the species present in the mercury(II) halide and thiocyanate systems, as a function of the free ligand concentration. Medium 1 M NH_4ClO_4 ; 25°C.
- Fig. 3. The total molar enthalpy change Δh_v as a function of the ligand number $\bar{n}$ for the mercury(II) halide systems in DMSO. The points refer to the values actually measured in the series of $C'_M = 4, 8$ and 16 mM (circles, squares and triangles, respectively; for the sake of clarity, those referring to the bromide system are filled). The fulldrawn curves have been calculated from the values of β_j and $\Delta H^\circ_{\beta j}$ determined (Tables 1 and 2). The curve of the thiocyanate system (from Fig. 4) has been included for comparison (dashed). Medium 1 M NH_4ClO_4 ; 25°C.
- Fig. 4. The total molar enthalpy change Δh_v as a function of the ligand number $\bar{n}$ for the mercury(II) thiocyanate system in DMSO, measured under the same conditions as for the halide systems (cf. Fig. 3). The curves of those systems have moreover been included for comparison.
- Fig. 5. The changes of free energy (white), enthalpy (black) and entropy (hatched) for the consecutive steps of the mercury(II) halide and thiocyanate systems in DMSO. Medium 1 M NH_4ClO_4 , 25°C.





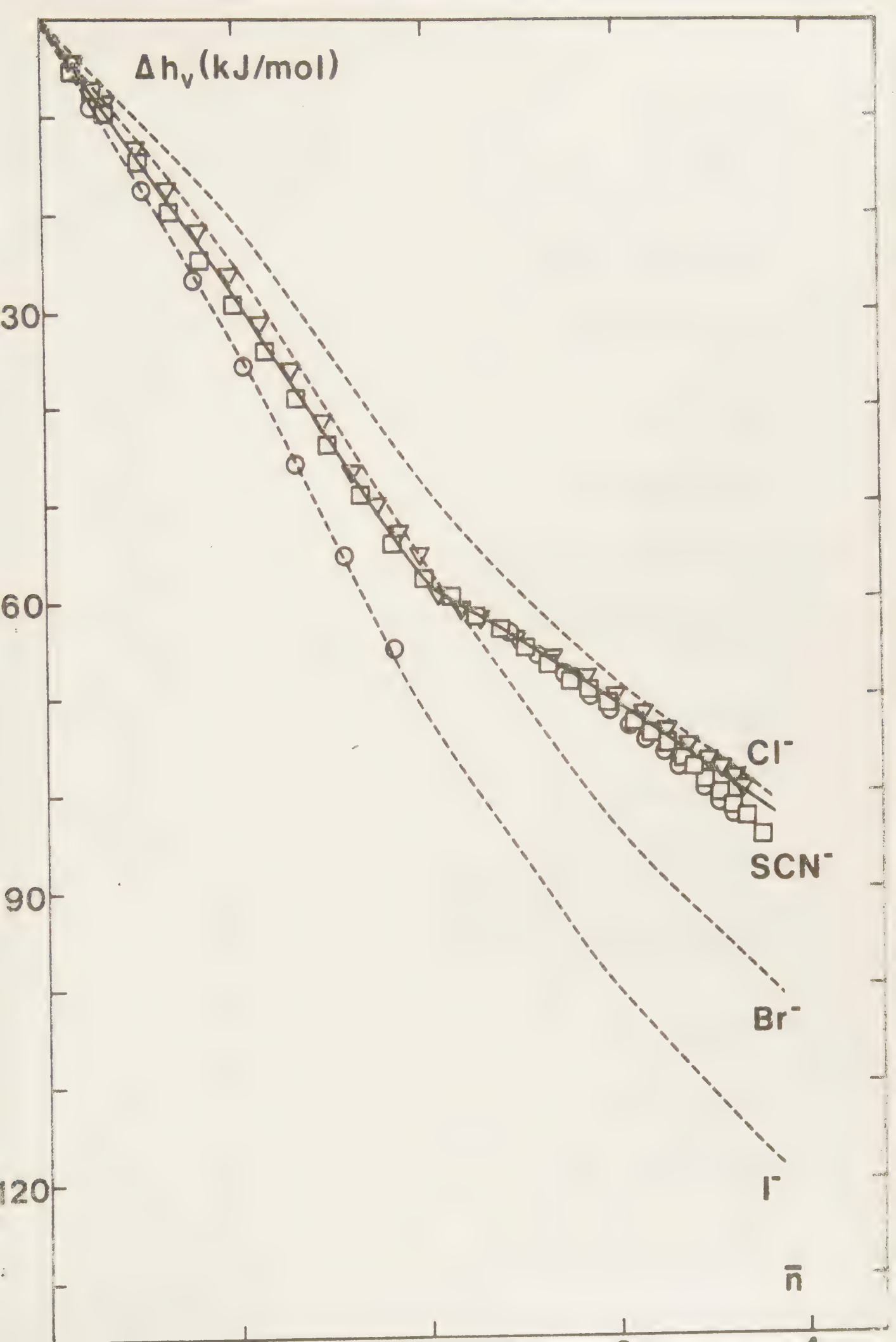




0

10

100



THE UNIVERSITY OF CHICAGO

152

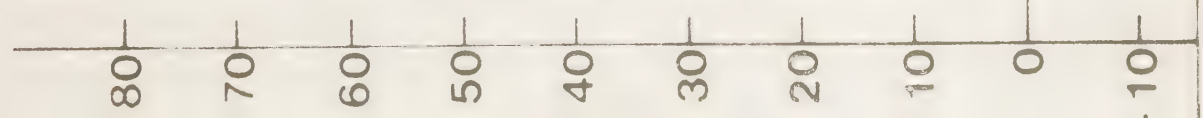
7 11

i

10

Cl^- | 1 | 2 | 3 | 4 | Br^- | 1 | 2 | 3 | 4 | I^- | 1 | 2 | 3 | 4 | SCN^- | 1 | 2 | 3 | 4 |

$-\Delta G_j^\circ, -\Delta H_j^\circ, T\Delta S_j^\circ / \text{kJ mol}^{-1}$



1. The first part of the paper discusses the importance of maintaining accurate records of all transactions.

2. The second part of the paper discusses the importance of maintaining accurate records of all transactions.

3. The third part of the paper discusses the importance of maintaining accurate records of all transactions.

4. The fourth part of the paper discusses the importance of maintaining accurate records of all transactions.

5. The fifth part of the paper discusses the importance of maintaining accurate records of all transactions.

6. The sixth part of the paper discusses the importance of maintaining accurate records of all transactions.

7. The seventh part of the paper discusses the importance of maintaining accurate records of all transactions.

8. The eighth part of the paper discusses the importance of maintaining accurate records of all transactions.

9. The ninth part of the paper discusses the importance of maintaining accurate records of all transactions.

10. The tenth part of the paper discusses the importance of maintaining accurate records of all transactions.

11. The eleventh part of the paper discusses the importance of maintaining accurate records of all transactions.

12. The twelfth part of the paper discusses the importance of maintaining accurate records of all transactions.

Acta Chem. Scand. Ser. A Reg. No.:

Text pages:

Received:

Other sheets:

Correspondence and proofs should be sent to

FK I. Persson, Oorganisk kemi 1, Kemicentrum, Box 740,
S-220 07 Lund.

Running title: Ahrland, Björk and Persson

Metal complexes in DMSO X

Metal Halide and Pseudohalide Complexes in Dimethyl Sulfoxide Solution X. Equilibrium and Enthalpy Measurements on Halide Systems of Zinc(II), Cadmium(II) and Mercury(II) in 0.1 M Ammonium Perchlorate.

STEN AHRLAND, NILS-OLOF BJÖRK and INGMAR PERSSON

Inorganic Chemistry 1, Chemical Center, University of Lund,
P.O. Box 740, S-220 07 Lund 7, Sweden.

The thermodynamics of the formation of zinc(II) bromide, cadmium(II) chloride, bromide and iodide, and mercury(II) bromide complexes in dimethyl sulfoxide (DMSO) has been studied in a 0.1 M ammonium perchlorate medium at 25°C. The stability constants have been determined potentiometrically and, except for the mercury(II) bromide, also calorimetrically, and the enthalpy changes calorimetrically. The complexes are more stable in the present medium than in the 1 M ammonium perchlorate employed previously. The overall enthalpy changes are less favourable than in 1 M ammonium perchlorate, but the overall entropy gains are considerably more favourable. The coordination changes take place at the same steps as in 1 M medium, except for the zinc(II) bromide. In this system, the switch from octahedral to tetrahedral coordination moves from the first to the second step as the concentration of NH_4^+ is decreased from 1 M to 0.1 M.

The thermodynamics of zinc(II), cadmium(II) and mercury(II) halide and thiocyanate complex formation in the aprotic solvent dimethyl sulfoxide (DMSO), has previously been investigated for the ionic medium 1 M ammonium perchlorate¹⁻⁵. It is of interest to investigate some of these systems at a lower concentration of ammonium perchlorate, in order to study the effects of a considerable quantitative change of the medium. The cadmium(II) halides have been chosen in order to examine how complexes formed by ligands of gradually changing bonding characteristics are influenced. By investigating also the zinc(II) and mercury(II) bromide systems, the effect on complexes of metal ions coordinating via bonds of different types can also be studied. The stability constants of the zinc(II) and cadmium(II) complexes have been determined both potentiometrically, by means of amalgam electrodes, and calorimetrically. A simultaneous determination of the stabilities, i.e. the free energy changes, and the heats of reaction by calorimetric measurements is possible only under certain conditions⁶ which are, however, met for these systems^{2,4}. For mercury(II) bromide they are not, however, so constants of this system have only been determined potentiometrically by means of the mercury electrode.

EXPERIMENTAL

Chemicals. The solvates $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$, $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$ and $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$, the ligand solutions and the amalgams used were prepared and analyzed as described previously^{1,7-9}.

Potentiometric measurements. The procedures used in the potentiometric measurements have been described elsewhere^{1,3,5}. As reference electrode the very stable and reproducible cadmium amalgam electrode has been used. The zinc and cadmium amalgam electrodes and the mercury electrode all follow Nernst's law. Their standard potentials for the medium used have been determined previously¹⁰. Three different values of the initial metal ion concentration were used in the potentiometric titrations, and each titration was repeated at least twice. The reproducibility was in general better than 0.3 mV for the

mercury(II) bromide and better than 0.4 mV for the zinc(II) and cadmium(II) halides. The emfs stayed constant within 0.5 mV for at least 15 hours.

The stability constants β_j were calculated from the potentiometric measurements by the computer program EMK¹¹, or for the reversed titrations used for the mercury(II) bromide system, by a modified version of this program. The formulas used in these programs have been long established^{12,13}.

In the zinc and cadmium systems, no experimental values were discarded in the final calculation of β_j . In the mercury bromide system, certain points had to be omitted, as will be further discussed below.

Calorimetric measurements. The calorimeter and the technique used have been described previously^{2,4,5,7,14,15}. The calibration constant ξ_v was the same as before⁵. The heats of dilution were determined by titrations where either the ligand or the central ion solution had been exchanged for pure ionic medium^{2,4,5}. In the mercury(II) bromide system it has moreover been possible to determine the heats of dilution of the intermediate complexes HgBr^+ , HgBr_2 and HgBr_3^- . These are around 60, 45 and 30%, respectively, of the heat of dilution of Hg^{2+} . Enthalpy changes and stability constants have been calculated from the calorimetric measurements by the program KALORI¹¹. For the final calculation of the enthalpy changes, the weighted means of the stability constants determined potentiometrically and calorimetrically were used.

Complete experimental data are available from the authors.

MEASUREMENTS AND RESULTS

Zinc(II) bromide. In the range of central ion and ligand concentrations used in the potentiometric measurements, viz. 2.5 mM $\leq C_M \leq 19.0$ mM, and $0 \leq C_L \leq 75.1$ mM respectively, the complex

formation is well described by three mononuclear complexes. Four complexes give about the same sum of least squares, but the error of the fourth stepwise constant K_4 is so large that the last complex remains hypothetical. No polynuclear complexes are formed in the ranges of C_M and C_L investigated. The results are in Table 1.

In the calorimetric measurements, the ranges of C_M and C_L used were $2.6 \text{ mM} \leq C_M \leq 16.2 \text{ mM}$ and $0 \leq C_L \leq 67.3 \text{ mM}$. Also these measurements indicate the formation of three mononuclear complexes. The values of β_j are listed in Table 1 as are the weighted means of the values found by the two methods employed. The complex formation function calculated from the mean constants is plotted in Fig. 1. The means were also used in the final calculation of the values of $\Delta H_{\beta_j}^\circ$ listed in Table 4. In Fig. 3, the total molar enthalpy change Δh_v is plotted as a function of the ligand number $\bar{n}$. The constants K_j , their ratios K_j/K_{j+1} , and the thermodynamic functions ΔG_j° , ΔH_j° and ΔS_j° of the consecutive steps, calculated from the values of β_j and $\Delta H_{\beta_j}^\circ$ finally adopted, are collected in Table 6.

Cadmium(II) chloride, bromide and iodide. In the potentiometric measurements, the concentration ranges used for the chloride system were $3.3 \text{ mM} \leq C_M \leq 19.6 \text{ mM}$ and $0 \leq C_L \leq 54.6 \text{ mM}$, for the bromide system $2.3 \text{ mM} \leq C_M \leq 19.6 \text{ mM}$ and $0 \leq C_L \leq 66.7 \text{ mM}$, and for the iodide system $1.3 \text{ mM} \leq C_M \leq 19.6 \text{ mM}$ and $0 \leq C_L \leq 75.0 \text{ mM}$. Within these ranges, four mononuclear complexes are formed in all the systems. No polynuclear complexes exist which is not surprising as such complexes are seemingly not formed even in very concentrated solutions¹⁶. The values of β_j are in Table 2.

In the calorimetric measurements, the range of concentration of cadmium(II) was $3.2 \text{ mM} \leq C_M \leq 19.7 \text{ mM}$, of chloride and bromide $0 \leq C_L \leq 59.1 \text{ mM}$, and of iodide $0 \leq C_L \leq 67.3 \text{ mM}$. Also by this method, four mononuclear complexes were found, and the values of β_j agree quite well with those found potentiometrically, Table 2. From the weighted means of β_j , Table 2, the complex formation curves plotted in Fig. 2 have been calculated, and also the final values of $\Delta H_{\beta_j}^\circ$, Table 4. In Fig. 4, Δh_v is given as a function of $\bar{n}$. The curves of the bromide system have also been entered in Figs. 1 and 3. The constants and thermodynamic functions referring to the consecutive steps are collected in Table 5, and, for the bromide system, also in Table 6.

Mercury(II) bromide. In the reversed titrations performed for this system, the mercury(II) and bromide concentrations were varied in the ranges $2.5 \text{ mM} \leq \underline{C}_M \leq 13.7 \text{ mM}$ and $8.0 \leq \underline{C}_L \leq 58.3 \text{ mM}$. The actual concentration of mercury(II) reacting with bromide was calculated from the equivalence points observed in the titrations and found to be 0.1 mM less than the formal concentration. This agrees with the results obtained earlier in 1 M ammonium perchlorate medium and confirms the conclusion drawn that the discrepancy is due to an impurity in the DMSO, with a very strong affinity for mercury(II)⁵. Experimental points of $\bar{n} < 1.66$ could not be made to fit, evidently on account of an incipient formation of mercury(I). These points were discarded. Four mononuclear complexes are found, with constants listed in Table 3. No polynuclear complexes are indicated; no such complexes are in fact formed even in much more concentrated solutions of this system^{17,18}. The complex formation function is given in Fig. 1.

The calorimetric measurements have been performed in the ranges $3.2 \leq \underline{C}_L \leq 15.7 \text{ mM}$ and $0 \leq \underline{C}_M \leq 56.6 \text{ mM}$. As the function Δh_v does not display any marked points of equivalence, Fig. 3, any correction of $\underline{C}_M$ was neither indicated, nor needed. The smooth course of Δh_v is due to the fact that the values of ΔH_j^0 do not differ very much between the consecutive steps, Table 6. The values of $\Delta H_{\beta j}^0$ are in Table 4, and the quantities calculated for the consecutive steps in Table 6.

DISCUSSION

In Tables 5 and 6, the equilibrium constants and thermodynamic functions of the consecutive steps, derived from the present measurements in 0.1 M ammonium perchlorate, are compared with those found previously in 1 M ammonium perchlorate¹⁻⁵.

The comparison between the cadmium(II) halide systems in the two media shows that the decrease of the ammonium perchlorate concentration causes a large increase of $\underline{K}_j$ (roughly ten times) for the chloride

complexes and a considerably smaller one for the bromide complexes. For the iodide complexes, a small increase is found for K_1 and K_2 , while K_3 and K_4 even show a slight decrease between the 1 M and the 0.1 M medium. In DMSO, the pattern is thus distinctly different for different halides. In a protic solvent like water, on the other hand, much the same pattern is found for chloride and iodide, at least in sodium perchlorate media¹⁹, and this pattern is moreover very similar to that found presently for iodide in DMSO. In these cases, the changes are of the magnitude to be expected as a consequence of the change of the activity conditions accompanying a decrease of the ionic strength from ≈ 1 M to ≈ 0.1 M. Especially for the chloride, but also for the bromide, the changes in DMSO between the two media are larger than expected, however. Most likely, this indicates a formation in DMSO of complexes between NH_4^+ and Cl^- and, to a lesser extent, between NH_4^+ and Br^- . Thus, NH_4Cl is not at all completely dissociated in DMSO at concentrations of NH_4^+ as high as 1 M, nor is NH_4Br .²⁰ On the other hand, NH_4I probably is, as are also all the sodium halides in water.

The complex formation follows the order of increasing electrostatic interaction, but considering the low charge density of NH_4^+ , a simple electrostatic interpretation seems hardly sufficient. This view is of course also supported by the fact that NaCl seems to be completely dissociated in water, in spite of the higher charge density of Na^+ compared with NH_4^+ . Most likely, the complex formation between NH_4^+ and Cl^- , or Br^- , in DMSO is mainly due to the hydrogen bonding properties of the ligands. In the aprotic solvent where no better partners are available, NH_4^+ will participate in those hydrogen bonds which would be formed e.g. in water between Cl^- , or Br^- , and the solvent molecules.

A comparison of the values of $\Delta H_{\beta 4}^\circ$ and $\Delta S_{\beta 4}^\circ$ shows that the overall stability increase between the two media is very much an entropy effect, Table 5. A general increase of the entropy gain as I decreases is certainly to be expected from the circumstance that a lower concentration of NH_4^+ means less order in the bulk solvent. The desolvation accompanying the formation of cadmium(II) halide complexes will then result in a larger total loss of order, and

hence in a more favourable entropy.

Such an increase of the entropy gain is generally accompanied by a less favourable enthalpy change, as part of the energy gained by solvation of medium ions is lost when I decreases. This partial compensation is very prominent for I^- . To some extent it also occurs for Br^- while for Cl^- the value of $\Delta H_{\beta 4}^{\circ}$ is much the same in both media. Evidently, in 1 M medium further reactions involving Cl^- , or Br^- , take place which make $\Delta H_{\beta 4}^{\circ}$ less favourable than it would otherwise be.²¹ These reactions are most likely the dissociation of NH_4Cl , or NH_4Br , which of course are much more extensive for 1 M than for 0.1 M concentration of NH_4^+ .

The values of ΔH_j° and ΔS_j° of the individual steps follow much the same pattern though the picture is somewhat blurred by changes in the relative magnitudes. Also in 0.1 M medium, the values of ΔS_2° are the most favourable of all ΔS_j° and those of ΔH_2° the most unfavourable, of all ΔH_j° . As in 1 M medium, the switch from octahedral to tetrahedral coordination thus mainly takes place at the second step, Table 5. The values of ΔS_3° and ΔH_3° are more prominent in 0.1 M than in 1 M medium, however, so the switch appears to be less clearcut in the more dilute medium.

For the zinc(II) and mercury(II) bromide complexes, similar increases of stability occur as in the case of the cadmium(II) bromide, Table 6. This proves of course that they are due to the ligand, and not to the metal ion involved, just as has been implied in the reasoning above.

As only three complexes are formed in the zinc system, $\Delta H_{\beta 3}^{\circ}$ and $\Delta S_{\beta 3}^{\circ}$ must be used for the comparison of the overall thermodynamics. As the switch to tetrahedral coordination has by then taken place in all the systems, the exclusion of the last step does not matter very much, however. The picture emerging is very similar for all the systems. A considerable increase of $\Delta S_{\beta 3}^{\circ}$ from 1 M to 0.1 M medium is to some extent compensated by more unfavourable values of $\Delta H_{\beta 3}^{\circ}$. It should be noted, however, that both effects are markedly larger for Hg(II) than for Cd(II) and Zn(II). In consideration of the huge

differences in strength and nature of the complexes, this rather modest difference in behaviour is perhaps not really surprising.

For the zinc(II) bromide system, the relative size of ΔS_1^0 and ΔS_2^0 changes between 1 M and 0.1 M medium, Table 6. The tendency found already for the cadmium(II) systems that the switch to tetrahedral coordination occurs at a later stage as the concentration of medium ions decreases, is thus so marked for zinc(II) bromide that the step of the main switch really changes. Considering that a higher concentration of medium ions ought to encourage the extra desolvation of the metal ion accompanying the change of coordination, it seems natural that the change should tend to occur at an earlier stage in the more concentrated medium, as is in fact the case. For the zinc(II) bromide system, the change from 1 M to 0.1 M medium means that its behaviour starts to resemble that found for the iodide and thiocyanate system already in 1 M medium.

Acknowledgements: Our thanks are due to Professor Roberto Portanova, University of Palermo, who performed part of the potentiometric titrations on the cadmium(II) systems. We gratefully acknowledge the support given to this project by the Swedish Natural Science Research Council.

REFERENCES

1. Ahrland, S. and Björk, N.O. Acta Chem. Scand. A 30 (1976) 249.
2. Ahrland, S. and Björk, N.O. Acta Chem. Scand. A 30 (1976) 257.
3. Ahrland, S. and Björk, N.O. Acta Chem. Scand. A 30 (1976) 265.
4. Ahrland, S., Björk, N.O. and Portanova, R. Acta Chem. Scand. A 30 (1976) 270.
5. Ahrland, S., Persson, I. and Portanova, R. To be published.
6. Cristensen, J.J., Ruckman, J., Eatough, D.J. and Izatt, R.M. Thermochim. Acta 3 (1972) 203.
7. Ahrland, S. and Björk, N.O. Acta Chem. Scand. A 28 (1974) 823.
8. Sandström, M., Persson, I. and Ahrland, S. Acta Chem. Scand. A 32 (1978) 607.
9. Persson, H. Acta Chem. Scand. 24 (1970) 3739.
10. Ahrland, S. and Persson, I. To be published.
11. Karlsson, R. and Kullberg, L. Chem. Scr. 9 (1976) 54.
12. Fronaeus, S. In Jonassen, H.B. and Weissberger, A. Eds., Technique of Inorg. Chem. Interscience, New York, London 1963, Vol. 1, Chapter 1.
13. Ahrland, S., Chatt, J., Davies, N.R. and Williams, A.A. J. Chem. Soc. (1958) 264.
14. Grenthe, I., Ots, H. and Ginstrup, O. Acta Chem. Scand. 24 (1970) 1067.
15. Ots, H. Acta Chem. Scand. 26 (1972) 3810.

16. Pocev, S., Triolo, R. and Johansson, G. Acta Chem. Scand. A 33 (1979) 179.
 17. Sandström, M. Acta Chem. Scand. A 32 (1978) 627
 18. Åhrland, S., Hansson, E., Iverfeldt, Å. and Persson, I.
To be published.
 19. Gerding, P. and Jönsson, I. Acta Chem. Scand. 22 (1968)
2247.
 20. Åhrland, S. and Björk, N.O. Coord. Chem. Rev. 16 (1975) 115.
 21. Åhrland, S. and Persson, I. To be published.
- .

Table 1. The overall stability constants (β_j/M^{-j}) of the zinc(II) bromide complexes in DMSO, ionic medium 0.1 M ammonium perchlorate, at 25°C. The constants have been determined potentiometrically and calorimetrically; the errors stated refer to three standard deviations. NP = number of points.

	Pot	Cal	Mean
β_1	74±26	71±57	73±27
β_2	(1.47±0.10)10 ⁵	(1.57±0.23)10 ⁵	(1.48±0.11)10 ⁵
β_3	(1.47±0.06)10 ⁷	(1.19±0.48)10 ⁷	(1.44±0.12)10 ⁷
NP	185	181	

Table 2. The stability constants (β_j/M^{-j}) of cadmium(II) chloride, bromide and iodide complexes in DMSO, ionic medium 0.1 M ammonium perchlorate, at 25°C. The constants have been determined potentiometrically and calorimetrically; the error refer to three standard deviations.

	Pot	Cal	Mean
Chloride			
β_1	$(2.36 \pm 0.37)10^4$	$(2.22 \pm 0.35)10^4$	$(2.29 \pm 0.25)10^4$
β_2	$(2.49 \pm 1.54)10^7$	$(1.71 \pm 0.54)10^7$	$(1.91 \pm 0.82)10^7$
β_3	$(5.79 \pm 1.05)10^{10}$	$(5.04 \pm 1.45)10^{10}$	$(5.48 \pm 0.80)10^{10}$
β_4	$(1.54 \pm 0.32)10^{13}$	$(0.88 \pm 0.31)10^{13}$	$(1.21 \pm 0.22)10^{13}$
NP	105	198	
Bromide			
β_1	4960±250	4480±800	4850±420
β_2	$(1.72 \pm 0.38)10^6$	$(1.15 \pm 0.72)10^6$	$(1.52 \pm 0.41)10^6$
β_3	$(2.90 \pm 0.15)10^9$	$(2.70 \pm 0.94)10^9$	$(2.87 \pm 0.47)10^9$
β_4	$(1.97 \pm 0.12)10^{11}$	$(1.67 \pm 1.26)10^{11}$	$(1.94 \pm 0.64)10^{11}$
NP	146	174	
Iodide			
β_1	386±31	330±75	370±41
β_2	$(1.87 \pm 1.12)10^4$	$(3.24 \pm 2.30)10^4$	$(2.32 \pm 1.28)10^4$
β_3	$(1.53 \pm 0.21)10^7$	$(1.72 \pm 0.41)10^7$	$(1.58 \pm 0.21)10^7$
β_4	$(1.87 \pm 0.31)10^8$	$(6.07 \pm 4.04)10^8$	$(2.15 \pm 2.02)10^8$
NP	122	174	

Table 3. The stability constants (β_j/M^{-j}) of the mercury(II) bromide complexes in DMSO, ionic medium = 0.1 M ammonium perchlorate, at 25°C. The constants have been determined potentiometrically; the errors refer to three standard deviations.

β_1	$(8.29 \pm 0.69) 10^{12}$
β_2	$(9.17 \pm 0.78) 10^{21}$
β_3	$(4.20 \pm 0.46) 10^{27}$
β_4	$(1.67 \pm 0.22) 10^{30}$
NP	361

Table 4. Overall enthalpy changes ($\Delta H_{\beta j}^{\circ}/\text{kJ mol}^{-1}$) for the formation of the zinc(II) bromide, cadmium(II) chloride, bromide, iodide and mercury(II) bromide systems in DMSO, ionic medium 0.1 M ammonium perchlorate, at 25°C. The errors stated refer to three standard deviations.

System	$\text{Zn}^{2+} - \text{Br}^-$	$\text{Cd}^{2+} - \text{Cl}^-$	$\text{Cd}^{2+} - \text{Br}^-$	$\text{Cd}^{2+} - \text{I}^-$	$\text{Hg}^{2+} - \text{Br}^-$
$-\Delta H_{\beta 1}^{\circ}$	$-(22.3 \pm 1.7)$	4.9 ± 0.2	0.9 ± 0.3	$-(5.2 \pm 0.3)$	20.0 ± 0.6
$-\Delta H_{\beta 2}^{\circ}$	$-(42.2 \pm 0.5)$	$-(7.5 \pm 0.8)$	$-(14.9 \pm 1.4)$	$-(26.8 \pm 2.6)$	44.1 ± 0.9
$-\Delta H_{\beta 3}^{\circ}$	$-(36.3 \pm 0.5)$	$-(14.0 \pm 0.3)$	$-(22.0 \pm 0.4)$	$-(33.3 \pm 0.5)$	68.5 ± 1.1
$-\Delta H_{\beta 4}^{\circ}$		1.5 ± 0.3	$-(10.6 \pm 0.6)$	$-(28.7 \pm 1.4)$	85.8 ± 1.4
NP	181	198	177	174	219

Table 5. Equilibrium constants (K_j/M^{-1}) and thermodynamic function (ΔG_j° , $\Delta H_j^\circ/kJ\ mol^{-1}$; $\Delta S_j^\circ/JK^{-1}mol^{-1}$) for the stepwise formation of cadmium(II) chloride, bromide and iodide complexes in DMSO at 25°C.

	0.1 M NH_4ClO_4			1 M $NH_4ClO_4^a$		
	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
$\log K_1$	4.36	3.69	2.57	3.23	2.92	2.18
$\log K_2$	2.92	2.50	1.80	1.97	1.91	1.37
$\log K_3$	3.46	3.28	2.83	2.58	2.75	2.93
$\log K_4$	2.34	1.83	1.13	1.75	1.68	1.18
K_1/K_2	27	16	5.9	18	10	6.4
K_2/K_3	0.29	0.17	0.09	0.24	0.15	0.03
K_3/K_4	13	28	58	6.7	12	58
$-\Delta G_1^\circ$	24.9	21.0	14.7	18.4	16.7	12.5
$-\Delta G_2^\circ$	16.7	14.7	10.3	11.2	10.9	7.8
$-\Delta G_3^\circ$	19.7	18.7	16.2	14.7	15.7	16.8
$-\Delta G_4^\circ$	13.4	10.4	6.1	10.0	9.5	6.7
$-\Delta H_1^\circ$	4.9	0.9	-5.2	6.3	3.9	-2.4
$-\Delta H_2^\circ$	-12.5	-15.8	-21.5	-15	-17	-27
$-\Delta H_3^\circ$	-6.7	-7.2	-6.6	-1	-2	5
$-\Delta H_4^\circ$	15.5	11.4	4.8	12.2	13	9.5
ΔS_1°	67	68	67	41	43	50
ΔS_2°	98	101	106	88	94	117
ΔS_3°	88	87	76	53	59	40
ΔS_4°	-7	-3	4	-7	-12	-10
$-\Delta H_{\beta 4}^\circ$	1.2	-10.7	-38.1	2	-2.1	-15
$\Delta S_{\beta 4}^\circ$	246	253	253	175	184	197

^aRef. 2.

Table 6. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j^O , $\Delta H_j^O/kJ\ mol^{-1}$; $\Delta S_j^O/JK^{-1}mol^{-1}$) for the stepwise of zinc(II), cadmium(II) and mercury(II) bromide complexes in DMSO at 25°C.

	0.1 M NH_4ClO_4			1 M $NH_4ClO_4^a$		
	Zn^{2+}	Cd^{2+}	Hg^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}
$\log K_1$	1.86	3.69	12.92	0.85	2.92	12.14
$\log K_2$	3.31	2.50	9.05	2.89	1.91	8.06
$\log K_3$	1.98	3.28	5.66	1.35	2.75	5.14
$\log K_4$		1.83	2.60		1.68	2.54
K_1/K_2	0.04	16	7.5×10^3	0.09	10	1.2×10^4
K_2/K_3	21	0.17	2.4×10^3	35	0.15	8.3×10^2
K_3/K_4		28	1.2×10^3		12	4.0×10^2
$-\Delta G_1^O$	10.6	21.0	73.7	4.8	16.7	69.3
$-\Delta G_2^O$	18.9	14.2	51.6	16.5	10.9	46.0
$-\Delta G_3^O$	11.3	18.7	32.3	7.7	15.7	29.3
$-\Delta G_4^O$		10.4	14.8		9.5	14.5
$-\Delta H_1^O$	-22.3	0.9	20.0	-27.8	3.9	24.7
$-\Delta H_2^O$	-19.9	-15.8	24.1	-9.1	-17	31.9
$-\Delta H_3^O$	5.9	-7.2	24.4	4.2	-2	27.8
$-\Delta H_4^O$		11.4	17.3		13	19.1
ΔS_1^O	110	68	180	110	43	149
ΔS_2^O	130	101	92	85	94	47
ΔS_3^O	18	87	26	12	54	5
ΔS_4^O		-3	-8		-12	-16
$-\Delta H_{\beta 3}^O$	-36.3	-22.1	68.5	-32.7	-15	84.4
$\Delta S_{\beta 3}^O$	258	256	298	207	196	201

^a Refs. 4 (Zn^{2+}), 2 (Cd^{2+}) and 5 (Hg^{2+}).

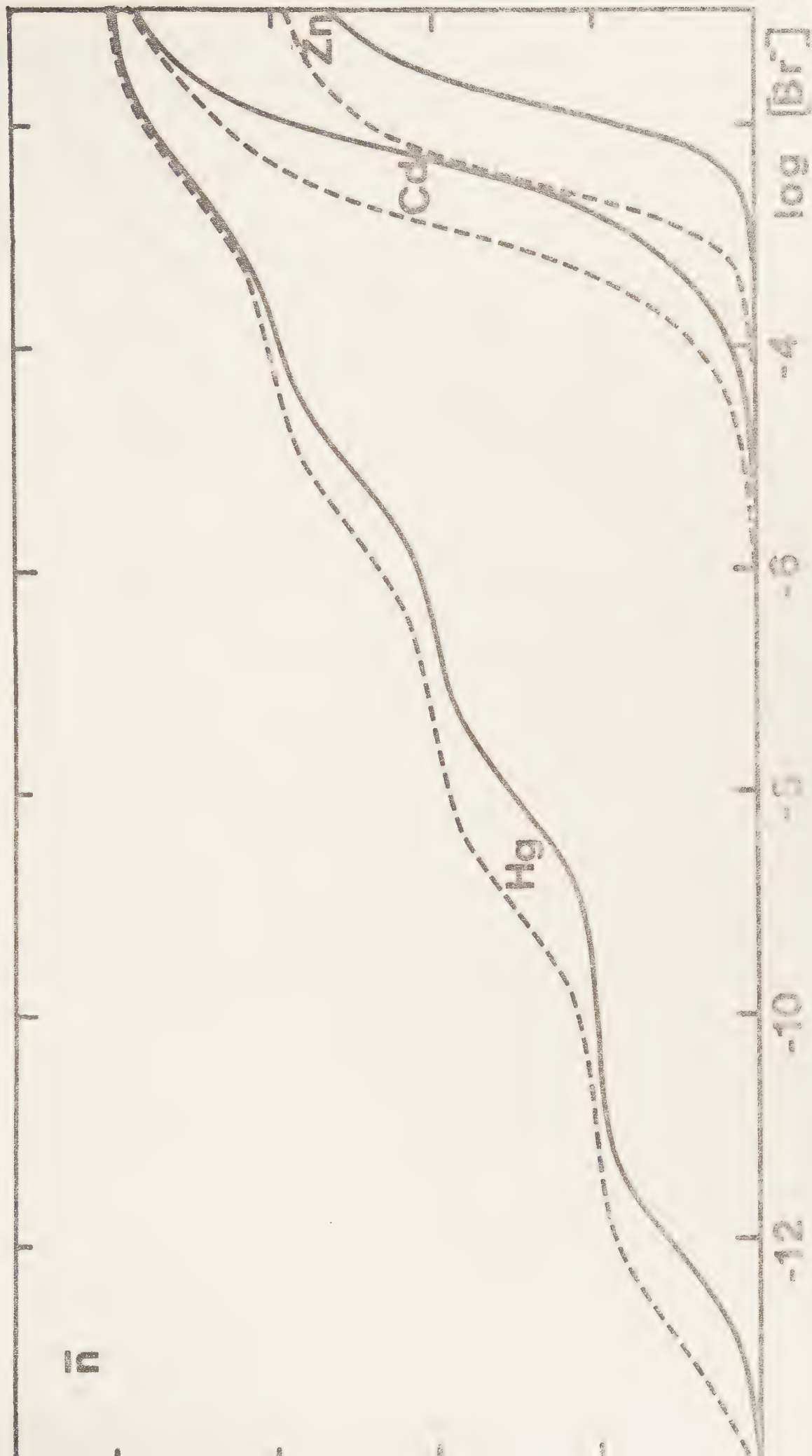
Text to the Figures.

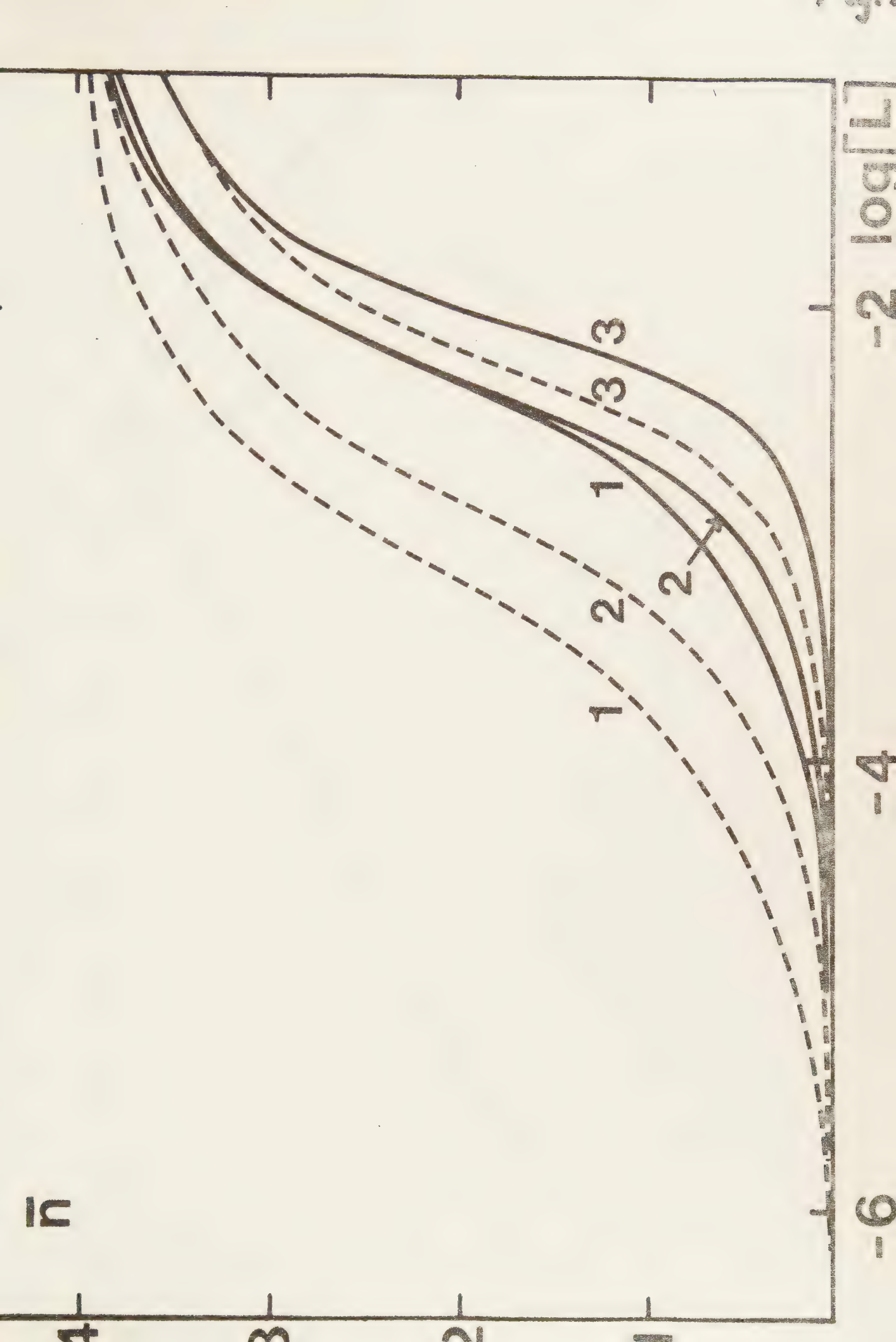
Fig.1. The complex formation functions of the zinc(II), cadmium(II) and mercury(II) bromide systems in DMSO, ionic media 0.1 M and 1 M ammonium perchlorate (dashed and solid curves, respectively).

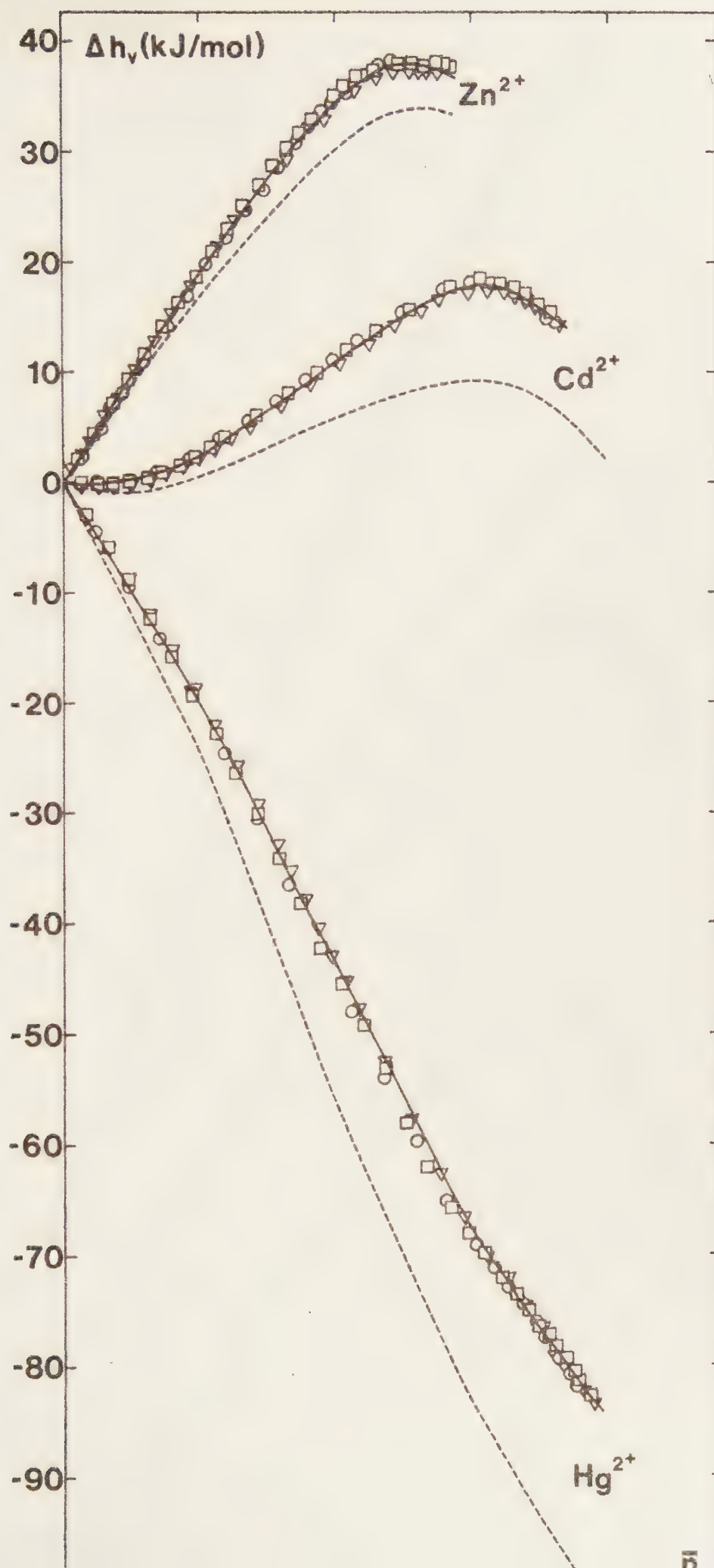
Fig.2. The complex formation functions of the cadmium(II) halide systems in DMSO, ionic media 0.1 M and 1 M ammonium perchlorate (dashed and solid curves, respectively). Ligands: chloride(1), bromide(2), iodide(3).

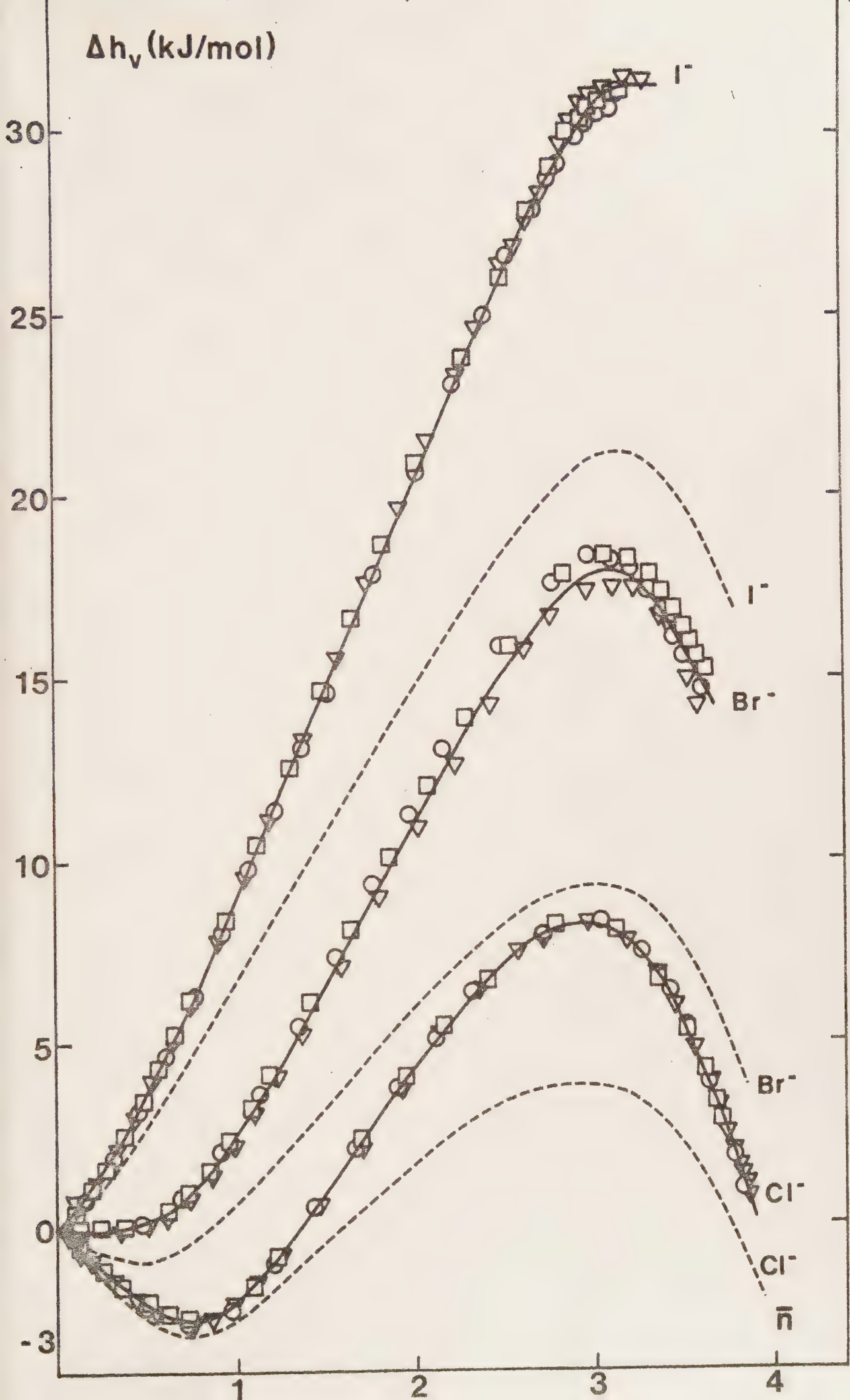
Fig.3. The total molar enthalpy change Δh_v as a function of the ligand number $\bar{n}$ for the zinc(II), cadmium(II) and mercury(II) bromide systems in DMSO at 25°C. The symbols refer to the present titrations in 0.1 M ammonium perchlorate at the initial concentrations $C_M^- = 4$ (O), 8 (□) and 16 mM (▽). The curves have been calculated from the values of β_j and $\Delta H_{\beta j}$ obtained in 0.1 M and 1 M ammonium perchlorate (solid and dashed, respectively).

Fig.4. The total molar enthalpy change Δh_v as a function of the ligand number $\bar{n}$ for the cadmium(II) chloride, bromide and iodide systems in DMSO, at 25°C. The symbols refer to the present titrations in 0.1 M ammonium perchlorate, at values of C_M^- stated in Fig.3. The curves have been calculated for 0.1 M and 1 M ammonium perchlorate (solid and dashed, respectively), as described in Fig.3.









Acta Chem. Scand. Ser. A Reg. No.:

Text pages: 14

Received:

Other sheets: 6

Correspondence and proofs should be sent to:

Fil.kand. Ingmar Persson, Oorganisk kemi 1, Kemicentrum,
Lunds Universitet, Box 740, S-220 07 Lund 7, Sverige

Running titles: Ahrland and Persson

Metal Complexes in DMSO XI

Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide
Solution. XI. Calorimetric measurements on the Zinc(II) and
Cadmium(II) Bromide Systems in Various Ionic Media.

STEN AHRLAND and INGMAR PERSSON

Inorganic Chemistry 1, Chemical Center, University of Lund,
P.O. Box 740, S-220 07 Lund 7, Sweden.

The thermodynamics of the formation of cadmium(II) and zinc(II) bromide complexes in various DMSO perchlorate media has been investigated calorimetrically. The complexes are more stable in Et_4N^+ , Li^+ and Na^+ media than in the NH_4^+ media previously used. This is probably due to an ion pair formation between NH_4^+ and Br^- . This interaction also causes exceptionally large differences between the stabilities in 0.1 M and 1 M NH_4^+ medium, much larger than those found between 0.1 M and 1 M Li^+ . The latter ones are of the magnitude expected from the difference in ionic strength. Thermodynamically, the stability decreases from the non-interacting medium ions to NH_4^+ , and from 0.1 M to 1 M media, are due to less favourable entropy terms. Those changes are partly compensated by more favourable enthalpy terms. These changes can be rationalized

by considering the ion pair formation, and the solvation of the medium cations.

In most DMSO media, a switch from octahedral to tetrahedral coordination takes place for cadmium(II) halides at the formation of the second complex. Rather remarkably, this switch is delayed to the third step in 0.1 M and 1 M lithium perchlorate.

The thermodynamics of zinc(II), cadmium(II) and mercury(II) halide complex formation in dimethylsulfoxide (DMSO) has previously been investigated in 1 M and, partly, also in 0.1 M ammonium perchlorate media.¹⁻⁵ It is of interest to investigate some of these systems in media containing other cations than NH_4^+ , especially as strong indications now exist that in aprotic solvents as DMSO, NH_4^+ is prone to form complexes with hydrogen bonding ligands.⁴ Consequently, the stability of chloride, and, to some extent, also bromide complexes would be lower in ammonium media than in media containing other cations. Besides this special effect, the general influence of large qualitative changes of the ionic medium on the complex formation is well worth investigating. Such data are largely missing for aprotic solvents which of course introduces an element of uncertainty into comparisons of results obtained in protic and aprotic solvents. Between e.g. water and DMSO large differences are generally found between the thermodynamic parameters of a certain system of complexes.²⁻⁴ One might ask how much of these differences that is in fact due to the solvent, and how much that can be accounted for by the different ionic media.

The ammonium perchlorate medium was introduced in the present investigations because it does not attack the amalgam electrodes^{1,2} used for the determination of the stabilities of the zinc(II) and cadmium(II) complexes. The amalgams are, on the other hand, rapidly oxidized by anhydrous lithium or sodium perchlorate. Especially in the case of zinc, the reaction is very fast. Neither are the amalgams stable in tetraethylammonium perchlorate. Also the pure mercury electrode is slowly attacked in these anhydrous perchlorate

solutions.⁵ If hydrated perchlorates are used, however, the oxidation is practically inhibited,³ for $\text{LiClO}_4 \cdot 3 \text{H}_2\text{O}$, or very slow, for $\text{NaClO}_4 \cdot \text{H}_2\text{O}$.

In most anhydrous perchlorate media, therefore, the stabilities of the complexes discussed cannot be measured potentiometrically by means of amalgam electrodes. In view of this, the results of some earlier investigations are questionable.⁶⁻¹¹ A comparison between different media necessitates another method of measurement.

If the stability constants are not too large (or too small) and moreover the enthalpy changes vary considerably between the consecutive steps, these parameters can be determined simultaneously with reasonable precision from calorimetric measurements.¹² Among the present systems, the zinc(II) and cadmium(II) bromides comply well with these conditions^{2,3} and have therefore been selected.

Cadmium(II) bromide has been most extensively studied, viz. in 0.1 M and 1 M lithium, 1 M sodium and 0.1 M tetrethylammonium perchlorate. Zinc(II) bromide has been studied only in 1 M sodium perchlorate. The temperature has been 25°C.

EXPERIMENTAL

Chemicals. The solvates $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ and $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$ were prepared and analyzed as described previously. The lithium solvate was prepared as follows: $\text{LiClO}_3 \cdot 3\text{H}_2\text{O}$ (1.0 mol) was dissolved in 400 ml (3.3 mol) 2,2-dimethoxypropane. After 2 hours 250 ml (3.5 mol) DMSO was added and the resulting mixture was shaken for 1/2 hour. The acetone and methanol formed, and the excess of 2,2-dimethoxypropane and DMSO were then evaporated at 100°C which took ≈2 hours. Analysis: Found: S: 25.9%, C: 21.2%, H: 5.73%; calculated for 2 DMSO: S: 24.4%, C: 18.3%, H: 4.61%. The compound thus contains somewhat more than 2 DMSO per lithium, corresponding to a formular $\text{LiClO}_4 \cdot 2.3\text{DMSO}$. It is extremely

hygroscopic and must be handled in dry atmosphere. $\text{NaClO}_4 \cdot 2\text{DMSO}$ was prepared as follows: $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (2.0 mol) was shaken with a mixture of 250 ml 2,2-dimethoxypropane (2.0 mol) and 300 ml DMSO (4.2 mol). A phase transformation took place which was complete in 1/2 hour. On cooling to 5°C , more crystals precipitated. The compound was collected on a Büchner funnel and then dried in vacuum under continuous pumping for 40 hours at room temperature. Analysis: Found: S: 22.4%; Calc: S: 23.0%. Lithium, sodium and tetraethylammonium bromide and tetraethylammonium perchlorate were dried in vacuum at 100°C . The bromide content was determined titrimetrically. The dimethylsulfoxide was purified as described elsewhere.¹³

Apparatus. The titration calorimeter used has been described previously.^{14,15}

Procedure. The technique and procedure have been described elsewhere.¹³ The initial metal concentrations were $C'_M = 5, 10$ and 20 mM and the ligand solution added contained the appropriate bromide of $C_L = 100$ or 500 mM. To all solution, perchlorate had been added so that the concentration of medium cations was 1 M. For the cadmium bromide system, totally six titration series were performed in each medium studied. For the zinc bromide system, totally twelve titrations were performed. The number of points measured for each medium, NP, is stated in Table 1. All titrations were carried out twice.

The calculations of the overall stability constants β_j and entropy changes $\Delta H_{\beta_j}^\circ$ have been performed by the computer program KALORI.¹⁶

The analysis were performed at the Department of Analytical Chemistry of this Chemical Center.

MEASUREMENTS AND RESULTS

Cadmium(II) bromide. In 0.1 M tetraethylammonium and 1 M sodium perchlorate, the ranges of cadmium(II) and bromide concentrations were $4.0 \text{ mM} \leq \underline{C}_M \leq 20.0 \text{ mM}$ and $0 \leq \underline{C}_L \leq 48.9 \text{ mM}$. Four mononuclear complexes are indicated, with the values of $\underline{\beta}_j$ and $\underline{\Delta H}_{\beta j}^{\circ}$ listed in Table 1. For reasons given below, the errors stated refer to a confidence limit of 95%, corresponding to 1.96σ . The precision achieved corresponds to a reproducibility in the individual points measured of $\lesssim 0.025 \text{ J}$. Under these conditions fairly precise values are obtained even for the fairly unstable CdBr_2 which never reaches 20% of $\underline{C}_M$, Fig 5.

In 0.1 M and 1 M lithium perchlorate, much the same ranges were used, viz. $4.0 \text{ mM} \leq \underline{C}_M \leq 20.0 \text{ mM}$ and $0 \leq \underline{C}_L \leq 46.8 \text{ mM}$. Also here four mononuclear complexes are indicated, but the random errors of $\underline{\beta}_j$ and $\underline{\Delta H}_{\beta j}^{\circ}$ are considerably larger than in the previous media, Table 1. This reflects a markedly poorer reproducibility of the individual points, viz. $\lesssim 0.045 \text{ J}$. Especially the errors in $\underline{\beta}_j$ become uncomfortably large, but within a confidence limit of 95% all values of $\underline{\beta}_j$ are nevertheless significant. Most of them are not, however, within the confidence limit 99.7%, corresponding to 3σ which has been applied in earlier measurements.¹⁻⁵

The total molar enthalpy change $\underline{\Delta h}_v$ is given as a function of the ligand number $\bar{n}$ in Fig. 1. The complex formation curve $\bar{n}(\log [\text{Br}^-])$ is given in Fig 3, and the distribution of the complexes $\underline{\alpha}(\log [\text{Br}^-])$ in Fig 5.

Zinc(II) bromide. In the 1 M sodium perchlorate medium used, measurements were performed in the ranges $4.0 \text{ mM} \leq \underline{C}_M \leq 19.8 \text{ mM}$ and $0 \leq \underline{C}_L \leq 180 \text{ mM}$. An excellent fit was obtained with three mononuclear complexes. Introduction of a fourth complex did not improve the fit. The values of $\underline{\beta}_j$ and $\underline{\Delta H}_{\beta j}^{\circ}$ obtained are listed in Table 1. The precision achieved corresponds to a reproducibility in the individual points of $\lesssim 0.035 \text{ J}$. Under these conditions, even the values of $\underline{\beta}_j$ and $\underline{\Delta H}_{\beta 1}$ are well determined, however, in

spite of the fact that the unstable ZnBr^+ at most reaches only $\approx 7\%$, Fig 6. The function $\Delta h_v(\bar{n})$, $\bar{n}(\log [\text{Br}^-])$ and $\alpha(\log [\text{Br}^-])$ are plotted in Figs. 2, 4 and 6 respectively.

DISCUSSION

Cadmium(II) bromide. The stability constants and thermodynamic functions derived for the consecutive steps from the values of β_j and $\Delta H_{\beta_j}^0$ collected in Table 1 are listed in Table 2. In this Table, the values determined previously in 0.1 M and 1 M ammonium perchlorate have also been entered.^{3,5}

As has been pointed out before,⁵ a stability increase larger than expected from the decrease of the ionic strength takes place between 1 M and 0.1 M ammonium perchlorate. This is most likely caused by a complex formation between NH_4^+ and Br^- which of course becomes much less extensive as the concentration of NH_4^+ is decreased. As this reaction is presumably due to a hydrogen bond formation $\text{NH}_4^+ - \text{Br}^-$, the cadmium(II) bromide complexes should be more stable in media where the medium cation cannot form such bonds. Moreover, the stability increase should be larger in 1 M than in 0.1 M media.

These effects are indeed all observed, Table 2. When 0.1 M NH_4^+ is exchanged for 0.1 M Et_4N^+ , of no ability to form hydrogen bonds, a further modest stability increase takes place. A similar increase is found if 0.1 M NH_4^+ is exchanged for 0.1 M Li^+ though in this case special effects occur which will be further discussed below. When 1 M NH_4^+ is exchanged for 1 M Na^+ , or 1 M Li^+ , the increases are much larger. Moreover, the difference between 0.1 M and 1 M Li^+ is much smaller than between 0.1 M and 1 M NH_4^+ . In the former case, the stabilities change about as much as is expected from the change in ionic strength.¹⁷ This difference between the NH_4^+ and the Li^+ media stands out very clearly in the complex formation curves, Fig 3.

In the NH_4^+ media, the very positive values of ΔS_2° and ΔH_2° indicate that the switch from the octahedral coordination represented by the solvate $\text{Cd}(\text{DMSO})_6^{2+}$ present initially¹⁸ to the certainly tetrahedral coordination¹⁹ of the finally formed CdBr_4^{2-} takes place at the formation of CdBr_2 . In 0.1 M Et_4N^+ and 1 M Na^+ medium the same pattern is found, Table 2. In the Li^+ media, on the other hand, this switch occurs at the formation of CdBr_3^- , as indicated by the large values of ΔS_3° and ΔH_3° . This difference between Li^+ on one hand and NH_4^+ , Et_4N^+ and Na^+ on the other is somewhat surprising. To judge from the solvation enthalpies,²⁰ Li^+ is the most strongly solvated among the medium cations concerned. One would therefore expect that Li^+ would tend to bring about the desolvation accompanying the switch of coordination more easily than the other ions, i.e. to cause the switch to take place at an earlier and not, as is in fact found, at a later step.

For the Li^+ media, the value of ΔH_3° are in fact so endothermic that the stability of CdBr_3^- becomes fairly low, in spite of the very positive ΔS_3° . While in the other media CdBr_2 is the only complex that never reaches a very large share of C_M , both CdBr_2 and CdBr_3^- are severely suppressed in the Li^+ media, Fig. 5. As a consequence, the complex formation curves are much steeper for the Li^+ media, Fig. 3.

The values of the overall enthalpy and entropy changes $\Delta H_{\beta 4}^{\circ}$ and $\Delta S_{\beta 4}^{\circ}$ show that the decreases of stability generally taking place between 0.1 M and 1 M media are due to less favourable values of $\Delta S_{\beta 4}^{\circ}$ in the more concentrated media, Table 2. These entropy losses are partly compensated by more favourable, i.e. less endothermic, values of $\Delta H_{\beta 4}^{\circ}$. Evidently, the increase of solvent order brought about by an increased ionic strength always causes a decrease of the entropy to be gained by complex formation. The break-up of the cadmium(II) solvates means a smaller entropy gain, the more well-ordered the surrounding medium. On the other hand, the more extensive solvate formation in the more concentrated medium means an energy gain which is reflected in a more favourable overall enthalpy term.

term, $\Delta S_{\beta 3}^{\circ}$, partly compensated by a less favourable enthalpy term, $\Delta H_{\beta 3}^{\circ}$. So far, the medium influence is the very similar for zinc(II) and cadmium(II) bromide.

The switch from octahedral to tetrahedral coordination takes place mainly at the formation of the second complex in 0.1 M NH_4^+ , but already at the formation of the first one in 1 M NH_4^+ . In this respect, 1 M Na^+ medium behaves as 0.1 M NH_4^+ , Table 3. One would perhaps rather expect that Na^+ , more strongly solvated than NH_4^+ , would rather encourage an early desolvation, with accompanying switch of coordination.

Obviously, the factors governing these coordination switches are still not sufficiently well known to warrant any safe predictions about the influence of various solvents and ionic media.

ACKNOWLEDGEMENT

We gratefully acknowledge the support given to this project by the Swedish Natural Science Research Council.

REFERENCES

- 1 Ahrland, S. and Björk, N.O. Acta Chem. Scand. A30 (1976) 265.
- 2 Ahrland, S., Björk, N.O. and Portanova, R. Acta Chem. Scand. A30 (1976) 270.
- 3 Ahrland, S. and Björk, N.O. Acta Chem. Scand. A30 (1976) 249, 257.
- 4 Ahrland, S., Persson, I. and Portanova, R. To be published.
- 5 Ahrland, S., Björk, N.O. and Persson, I. To be published.
- 6 Samoilenko, V.M. and Lyashenko, V.I. Zh. Neorg. Kim. 18 (1973) 2968
- 7 Pool, K. J. Polarogr. Soc. 13 (1967) 23.
- 8 Samoilenko, V.M. Lyashenko, V.I. and Polishchuk, N.V. Zh. Neorg. Khim. 19 (1974) 2984.
- 9 Burrus, R.T. Polarographic studies in dimethyl sulfoxide Diss., University of Tennessee, 1962.
- 10 Balyatinskaya, L.N. Zh. Neorg. Khim 20 (1975) 3210.
- 11 Foll, A., Le Demezet, M. and Courtot-Coupez, J. Bull. Soc. Chim. Fr. (1972) 1207.
- 12 Christensen, J.J., Ruckman, J., Eatough, D.J. and Izatt, R.M. Thermochim. Acta 3 (1964) 203.
- 13 Ahrland, S. and Björk, N.O. Acta Chem. Scand. A28 (1974) 823.
- 14 Grenthe, I., Ots, H. and Ginstrup, O. Acta Chem. Scand. 24 (1970) 1067.
- 15 Ots, H. Acta Chem. Scand. 26 (1972) 3810.
- 16 Karlsson, R. and Kullberg, L. Chem. Scr. 9 (1976) 54.
- 17 Gerding, P. Acta Chem. Scand. 22 (1968) 1283.
- 18 Sandström, M., Persson, I. and Ahrland, S. Acta Chem. Scand. A32 (1978) 607.
- 19 Pocev, S., Triolo, R. and Johansson, G. Acta Chem. Scand. A33 (1979) 179.
- 20 Ahrland, S. Pure Appl. Chem. 51 (1979) 2019.

Table 1. Overall stability constants (β_j/M^{-j}) and overall enthalpy changes ($\Delta H_{\beta j}/\text{kJmol}^{-1}$) for the formation of cadmium(II) bromide complexes in various DMSO media, at 25°C.
 The errors refer to a 95% confidence limit. NP denotes number of observations (aliquotes added) for each system.

$\text{Cd}^{2+} - \text{Br}^-$		$\text{Zn}^{2+} - \text{Br}^-$			
	0.1 M Et_4N^+	1 M Na^+	1 M Li^+	0.1 M Li^+	1 M Na^+
β_1	$(8.3 \pm 0.8) \cdot 10^3$	$(3.0 \pm 0.3) \cdot 10^3$	$(3.6 \pm 1.1) \cdot 10^3$	$(6.1 \pm 2.2) \cdot 10^3$	36 ± 10
β_2	$(6.4 \pm 1.6) \cdot 10^6$	$(6.9 \pm 2.0) \cdot 10^5$	$(3.0 \pm 2.1) \cdot 10^6$	$(7.2 \pm 4.6) \cdot 10^6$	$(4.6 \pm 0.2) \cdot 10^4$
β_3	$(1.6 \pm 0.4) \cdot 10^{10}$	$(1.0 \pm 0.2) \cdot 10^9$	$(2.7 \pm 1.9) \cdot 10^9$	$(8.0 \pm 6.6) \cdot 10^9$	$(5.2 \pm 0.4) \cdot 10^6$
β_4	$(2.6 \pm 1.1) \cdot 10^{12}$	$(7.4 \pm 0.3) \cdot 10^{10}$	$(6.0 \pm 5.6) \cdot 10^{12}$	$(1.0 \pm 1.0) \cdot 10^{13}$	
$-\Delta H_{\beta 1}$	0.0 ± 0.2	2.8 ± 0.2	0.3 ± 0.3	$-(0.3 \pm 0.3)$	$-(23.7 \pm 2.7)$
$-\Delta H_{\beta 2}$	$-(17.9 \pm 1.2)$	$-(10.8 \pm 1.8)$	$-(2.8 \pm 2.7)$	$-(4.2 \pm 2.0)$	$-(43.1 \pm 0.6)$
$-\Delta H_{\beta 3}$	$-(25.3 \pm 0.5)$	$-(17.4 \pm 0.8)$	$-(26.7 \pm 9.3)$	$-(31.7 \pm 5.0)$	$-(36.3 \pm 0.2)$
$-\Delta H_{\beta 4}$	$-(15.7 \pm 0.5)$	$-(4.0 \pm 1.3)$	$-(16.2 \pm 0.5)$	$-(20.8 \pm 0.5)$	
NP	120	120	102	112	188

Table 2. Stability constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJmol^{-1}$; $\Delta S_j^\circ/JK^{-1}mol^{-1}$) for the stepwise formation of cadmium(II) bromide complexes in various DMSO perchlorate media, at 25°C.

	1 M NH_4^+	0.1 M NH_4^+	0.1 M EtN_4^+	1 M Na^+	1 M Li^+	0.1 M Li
$\log K_1$	2.92	3.69	3.92	3.48	3.56	3.79
$\log K_2$	1.91	2.50	2.88	2.36	2.93	3.07
$\log K_3$	2.75	3.28	3.40	3.17	2.94	3.05
$\log K_4$	1.68	1.83	2.21	1.85	3.35	3.11
K_1/K_2	10	16	11	13	4.3	5.3
K_2/K_3	0.15	0.17	0.30	0.15	0.96	1.03
K_3/K_4	11.8	28	16	21	0.39	0.88
$-\Delta G_1^\circ$	16.7	21.0	22.4	19.9	20.3	21.6
$-\Delta G_2^\circ$	10.9	14.2	16.5	13.5	16.7	17.5
$-\Delta G_3^\circ$	15.7	18.7	19.4	18.1	16.8	17.4
$-\Delta G_4^\circ$	9.5	10.4	12.6	10.6	19.1	17.7
$-\Delta H_1^\circ$	3.9	0.9	0.0	2.8	0.3	-0.3
$-\Delta H_2^\circ$	-17	-15.8	-17.9	-13.6	-3.1	-4.0
$-\Delta H_3^\circ$	-2	-7.2	-7.3	-6.6	-23.9	-27.5
$-\Delta H_4^\circ$	13	11.4	9.5	13.4	10.5	10.9
ΔS_1°	43	68	75	57	67	73
ΔS_2°	94	101	115	91	66	72
ΔS_3°	59	87	90	83	137	151
ΔS_4°	-12	-3	10	-9	29	23
$-\Delta H_{\beta 4}^\circ$	-2	-10.6	-15.7	-4.0	-16.2	-20.8
$\Delta S_{\beta 4}^\circ$	184	252	290	221	299	319

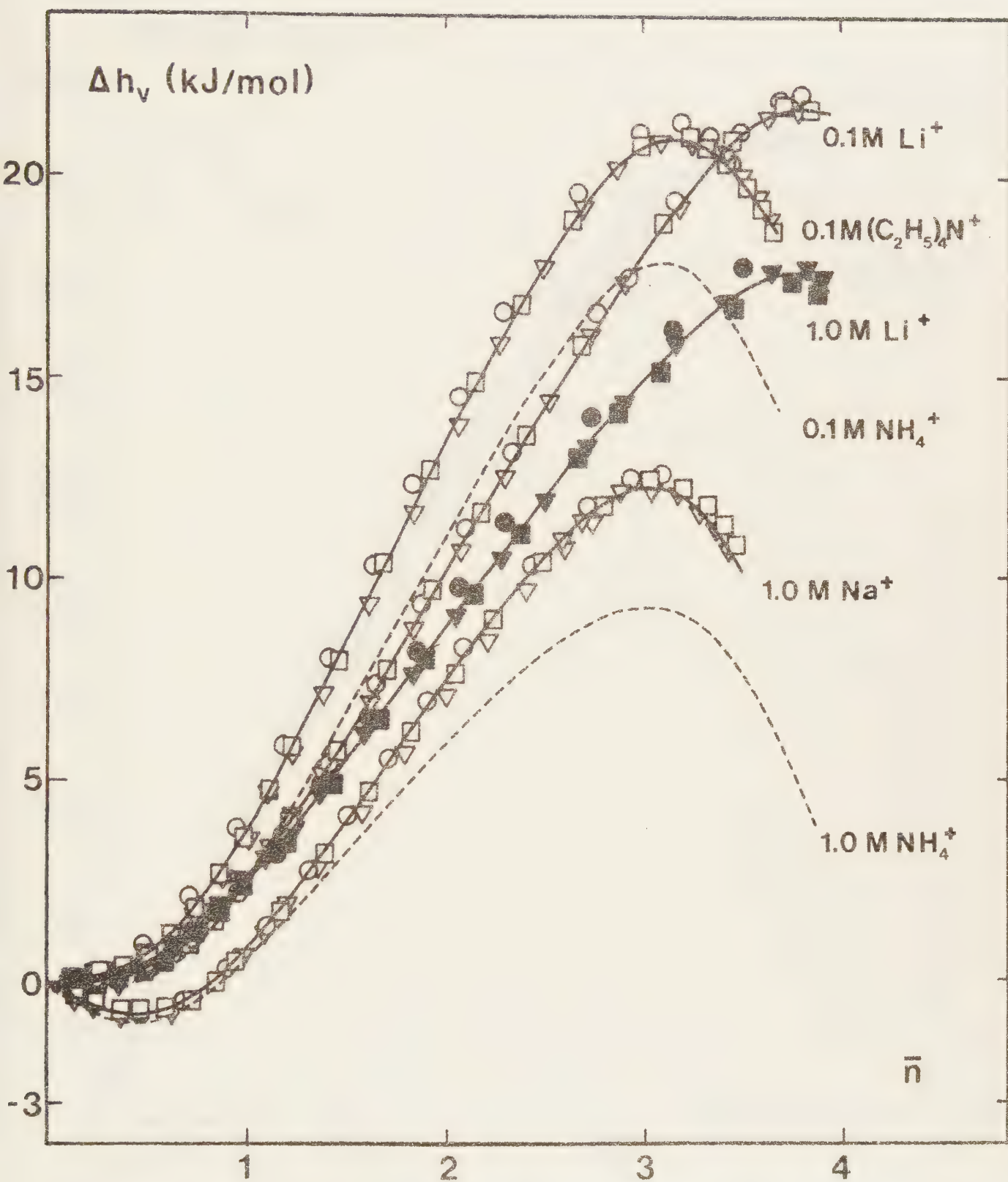


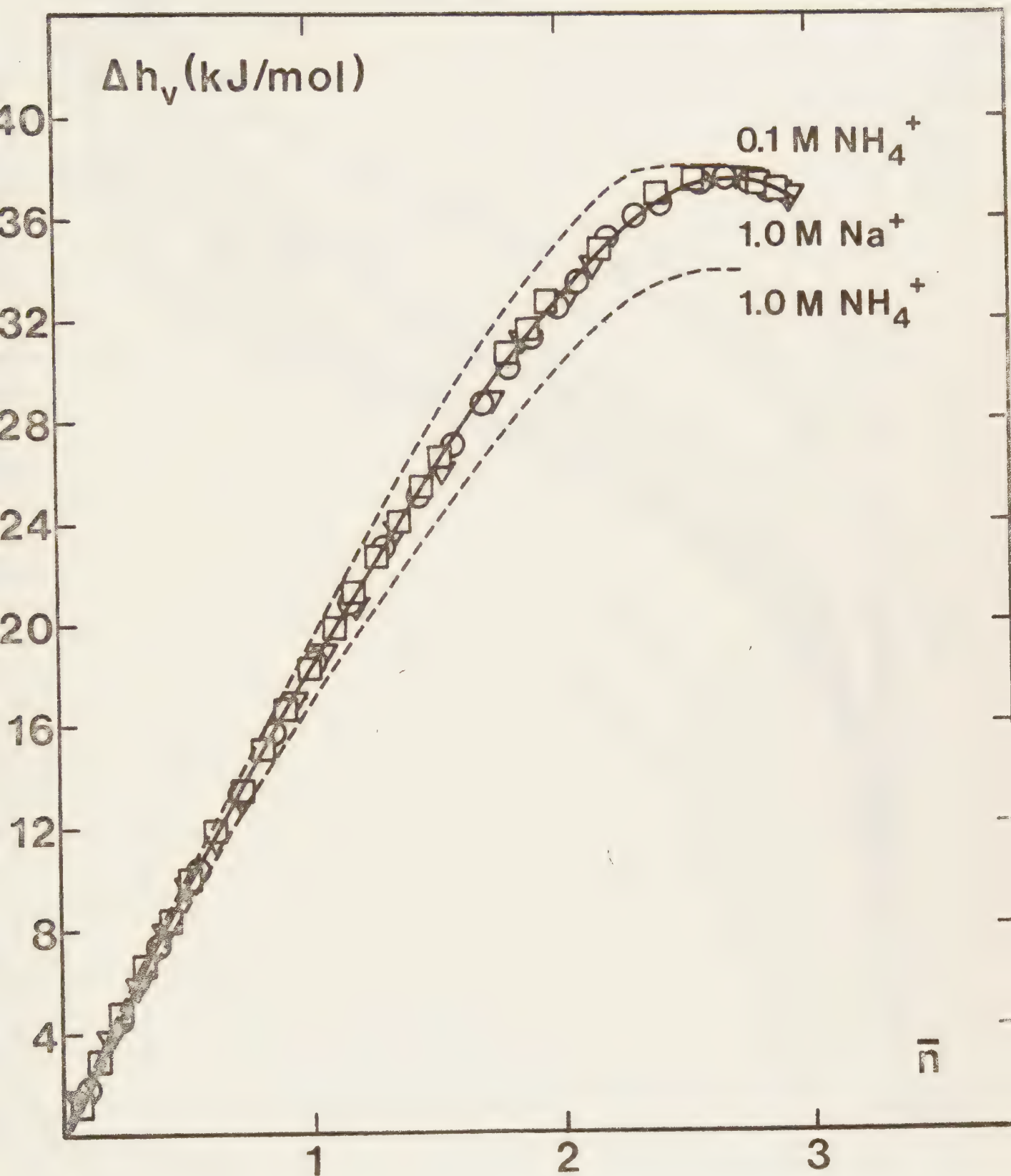
Table 3. Stability constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJmol^{-1}$; $\Delta S_j^\circ/JK^{-1}mol^{-1}$) for the stepwise formation of zinc(II) bromide complexes in various DMSO perchlorate media, at 25°C.

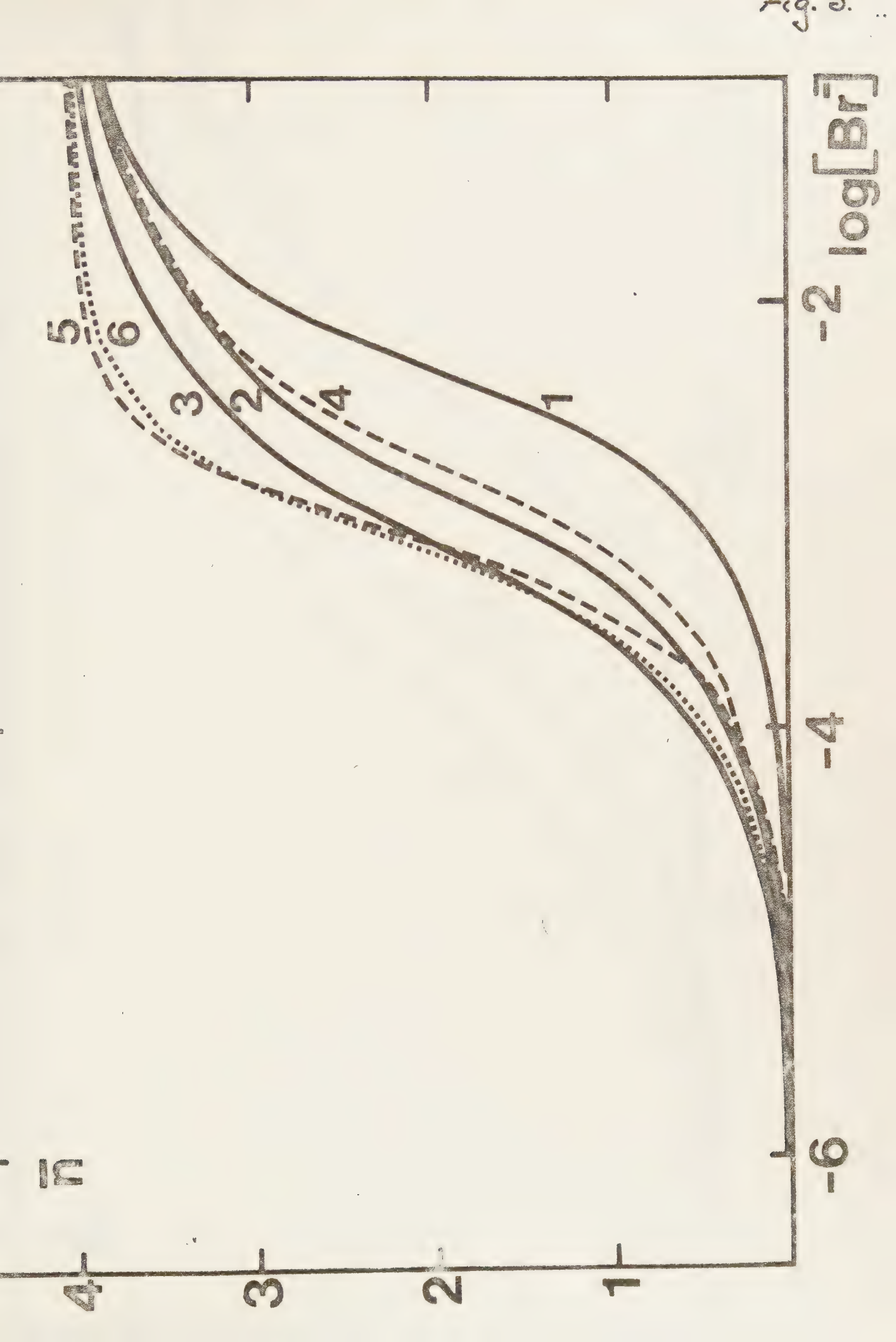
	1 M NH_4^+	0.1 M NH_4^+	1 M Na^+
$\log K_1$	0.85	1.86	1.56
$\log K_2$	2.89	3.31	3.11
$\log K_3$	1.35	1.98	2.05
K_1/K_2	0.009	0.036	0.028
K_2/K_3	35	21	11
$-\Delta G_1^\circ$	4.8	10.6	8.9
$-\Delta G_2^\circ$	16.5	18.9	17.7
$-\Delta G_3^\circ$	7.7	11.3	11.7
$-\Delta H_1^\circ$	-27.8	-22.3	-23.4
$-\Delta H_2^\circ$	-9.1	-19.9	-19.7
$-\Delta H_3^\circ$	4.2	5.9	6.8
ΔS_1°	110	110	108
ΔS_2°	85	130	126
ΔS_3°	12	18	16
$-\Delta H_{\beta 4}^\circ$	-32.7	-36.3	-36.3
$\Delta S_{\beta 4}^\circ$	207	259	250

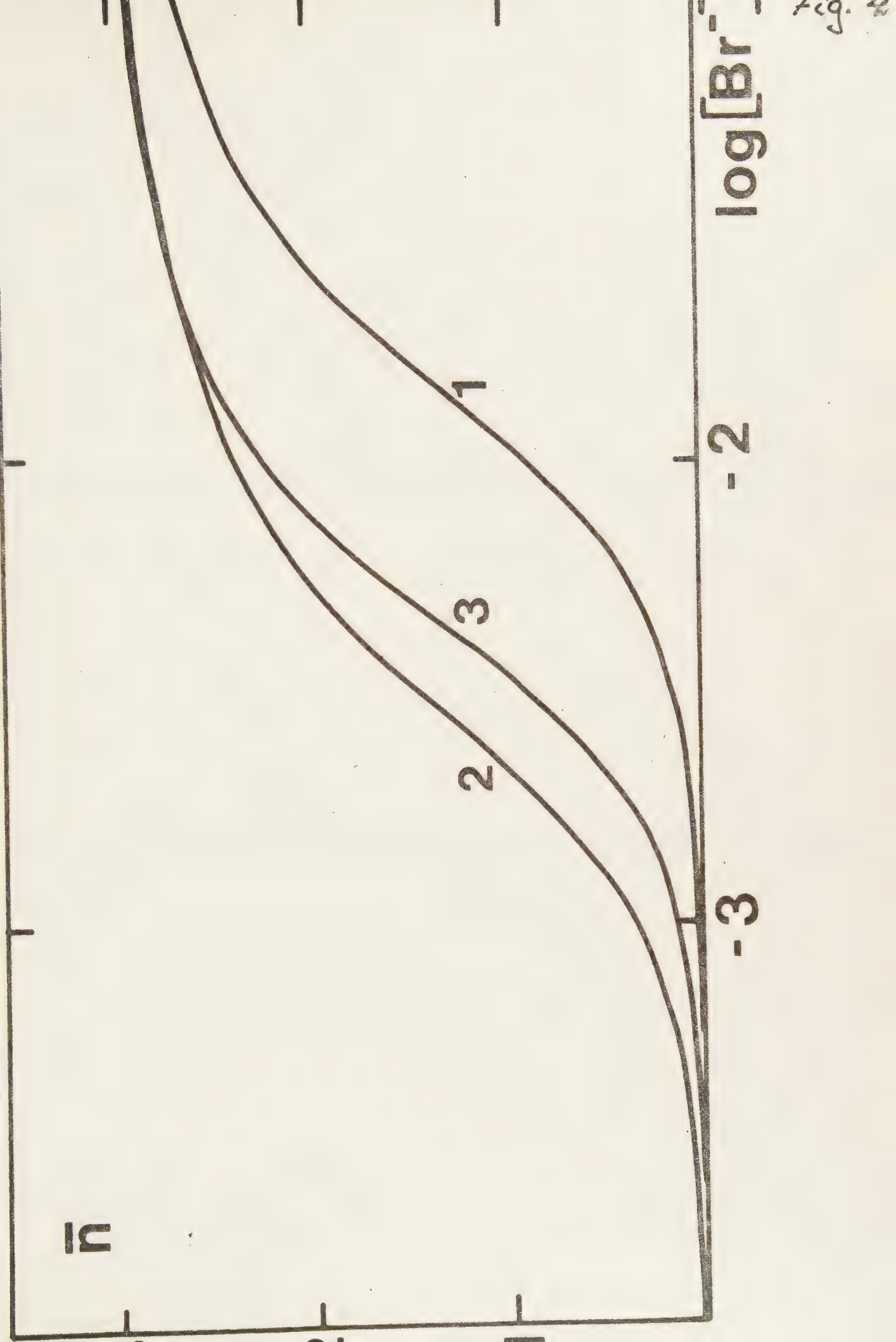
Text to Figures:

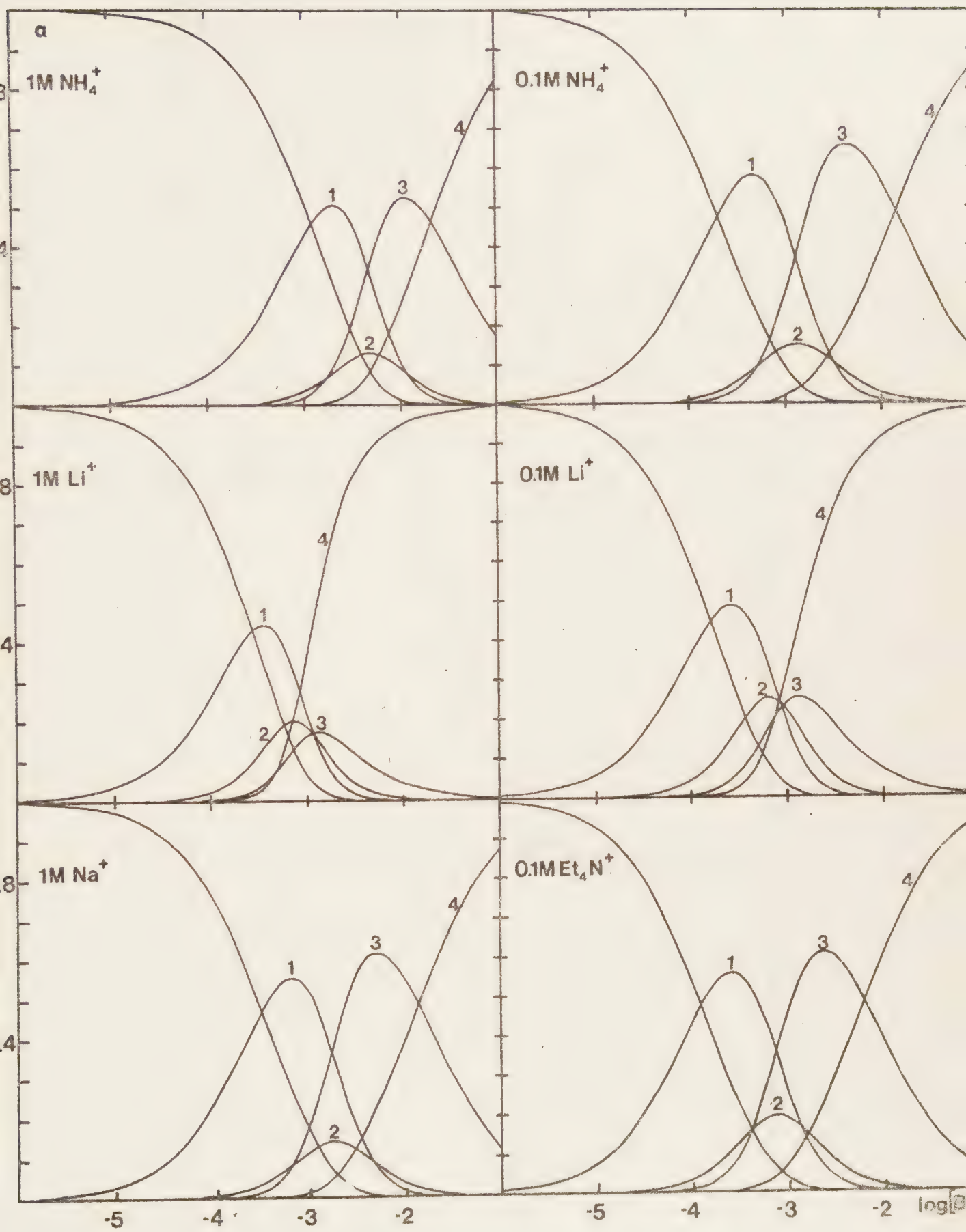
- Fig. 1 The total molar enthalpy change Δh_v as a function of $\bar{n}$ for the cadmium bromide system in various perchlorate media. The symbols refer to the initial concentrations $C'_M = 5$ (○), 10 (□), and 16 mM (▽), in the present measurements. The solid curves have been calculated from the values of β_j and $\Delta H_{\beta j}^\circ$ found. Dashed curves refer to previous measurements in 0.1 M and 1 M NH_4^+ media.
- Fig. 2 The total molar enthalpy change Δh_v as a function of $\bar{n}$ for the zinc(II) bromide system in various perchlorate media. The symbols refer to the initial concentrations $C'_M = 5$ (○), 10 (□) and 20 mM (▽) in 1 M Na^+ medium. The solid curve has been calculated from the values of β_j and $\Delta H_{\beta j}^\circ$. Dashed curves refer to previous measurements in 0.1 M and 1 M NH_4^+ media.
- Fig. 3 The complex formation functions of the cadmium(II) bromide system in the perchlorate media 1 M NH_4^+ (1), 0.1 M NH_4^+ (2), 0.1 M Et_4N^+ (3), 1 M Na^+ (4), 1 M Li^+ (5) 0.1 M Li^+ (6).
- Fig. 4 The complex formation functions of the zinc(II) bromide system in the perchlorate media 1 M NH_4^+ (1), 0.1 M NH_4^+ , 1 M Na^+ (3).
- Fig. 5 The complex distribution functions of the cadmium(II) bromide system in the ionic media investigated.
- Fig. 6 The complex distribution functions of the zinc(II) bromide system in the ionic media investigated.

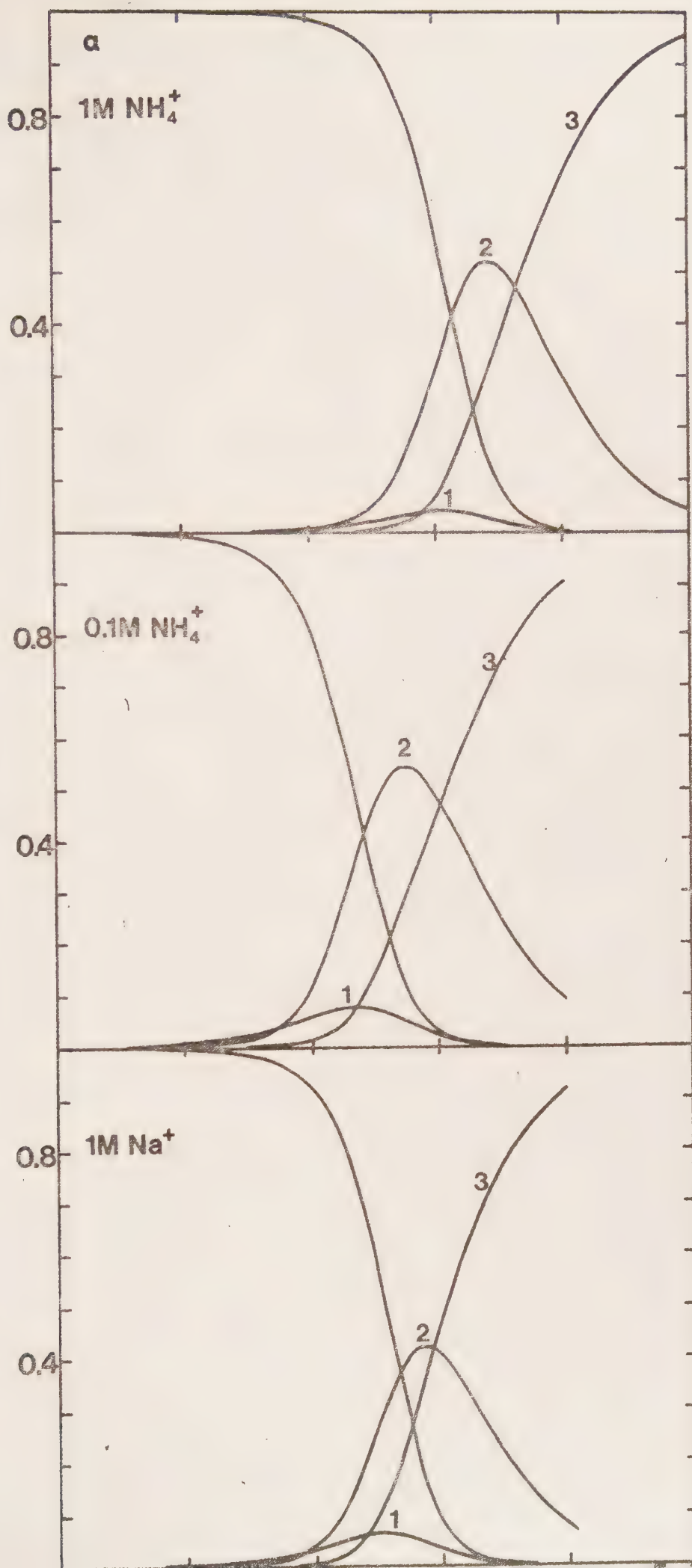












the *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM).

The *Journal of the American Medical Association* (JAMA) is a peer-reviewed medical journal that publishes research, clinical practice, and public health information.

The *New England Journal of Medicine* (NEJM) is a peer-reviewed medical journal that publishes research, clinical practice, and public health information.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

The *Journal of the American Medical Association* (JAMA) and the *New England Journal of Medicine* (NEJM) are both highly respected medical journals.

On the Coordination around Mercury(II), Cadmium(II) and Zinc(II) in Dimethyl Sulfoxide and Aqueous Solutions. An X-Ray Diffraction, Raman and Infrared Investigation

MAGNUS SANDSTRÖM,^a INGMAR PERSSON^b and STEN ÅHRLAND^b

^a Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden and

^b Inorganic Chemistry I, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden

The structures of the solvated metal ions in dimethyl sulfoxide (DMSO) solutions of mercury(II) and cadmium perchlorates have been determined by X-ray diffraction measurements. In both cases, regularly octahedral hexasolvates are formed, with DMSO coordinated *via* the oxygen atom. The bond lengths are: Hg–O 2.393(5), Cd–O 2.292(4) Å. The value of Hg–O is significantly longer than in the solid hexasolvate, while that of Cd–O is virtually the same in both phases. The bond angles Hg–O–S, 120.2(1.0)° and Cd–O–S, 125.7(1.0)°, are not significantly different from the average angles found in the solid solvates. A recalculation of earlier X-ray diffraction data pertaining to mercury(II) perchlorate in aqueous solution confirms that the hydrate formed is indeed regularly octahedral. The bond length Hg–O is 2.41(1) Å, *i.e.* close to the value found in DMSO solution. These bond lengths correspond to octahedral ionic radii of Cd²⁺ and Hg²⁺ of 0.94 and 1.05 Å, respectively.

The Raman spectra of perchlorate solutions of mercury(II), cadmium and zinc in DMSO confirm that the metal ions are all coordinated *via* oxygen. The spectra also reflect the change in character of the M–O bond from mercury(II) to zinc. Both the decreasing covalency and the increasing electrostatic interaction are clearly indicated.

In the aprotic solvent dimethyl sulfoxide (DMSO), the neutral mercury halides HgCl₂, HgBr₂ and HgI₂ are all easily soluble.^{1,2a} In the solvated HgX₂ molecules, the angles X–Hg–X (X=Cl, Br, I) deviate significantly² from the value 180° found in the gaseous and solid halides (except for red HgI₂).^{3,4} On the addition of excess halide further

ligands are taken up, resulting in the formation of HgX₃[–] and finally, HgX₄^{2–}. The HgI₃[–] and HgBr₃[–] ions are pyramidal, slightly flattened relative to a regularly tetrahedral arrangement.¹ In all the systems the fourth complex is a regular tetrahedron.^{1,2}

In aqueous solution, the complexes HgX₂ should be less bent than in DMSO, on account of the weaker interaction with the solvent,^{4,5} but the solubilities in this protic solvent are too low for a structure determination by X-ray diffraction. The complexes HgBr₃[–] and HgI₃[–] are again slightly flattened pyramids, derived from tetrahedra.⁶ As in DMSO, the mononuclear complexes HgX₄^{2–} finally formed are all regular tetrahedra.^{6,7}

In the numerous solid compounds where linear HgX₂ units exist, four longer contacts usually complete a distorted octahedral coordination around Hg.^{2b,3,8–15} Planar HgX₃[–], with two long contacts forming a trigonal bipyramid,^{16–21} pyramidal HgX₃[–], with a bridging X atom completing a distorted tetrahedral coordination,^{22–24} and tetrahedral HgX₄^{2–},^{25–29} also exist in solid state. Even discrete bipyramids HgCl₅^{3–} have been found.³⁰

Both in water and in DMSO, the formation of the third complex thus involves a drastic change of the digonal coordination characteristic of the second complex. In the case of bromide and iodide, the new arrangements very probably are approximately tetrahedral, while the picture is less clear for the chloride complexes.

Another drastic change of coordination very probably occurs in both solvents, as the digonal

second complex is formed when halide is added to a solution of the solvated mercury(II) ion. The solvated perchlorates $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$ have been crystallized, the structures of which contain octahedrally coordinated solvate ions as discrete entities.^{31,32} It is therefore very plausible that such species exist also in solution. In aqueous perchlorate solution, the existence of the hexahydrate has in fact been proved by X-ray diffraction measurements.³³

In aqueous solution, the switch from digonal to tetrahedral coordination at the formation of the third complex is also clearly indicated by abrupt changes of the magnitude of the enthalpy changes ΔH_j° of the consecutive formation reactions. These become much less exothermic for the two later steps.³⁴

Changes of ΔS_j° also occur, but they are not clear-cut enough to yield further evidence.³⁴ As to the postulated change from an initial octahedral coordination to an intermediate digonal one, relatively little can be learned from the thermodynamic data. Neither ΔH_j° , nor ΔS_j° differ very drastically between the first and second step. This must mean that water molecules are expelled from the close vicinity of the mercury atoms at both stages. The first ligand displaces one water molecule and loosens the bonds of the others except the one in *trans* position to the ligand which might be held even more tightly than before.³³ This is supported by the high acidities of the HgX^+ and HgOH^+ species compared with the acidity of the Hg^{2+} ion.³⁵ The second ligand replaces this water molecule and relegates the remaining ones to even more distant positions. Under such conditions, the thermodynamic functions of the first two steps need not be very different. The hydration of the HgX_2 complexes is indeed quite weak as is shown by their low heats of solvation.³⁶

In DMSO, the thermodynamics of the formation of mercury(II) halide complexes follows a pattern which is quite different from that found in water. The values of ΔH_j° do not vary much between the different halides or, perhaps even more remarkable, between the consecutive steps.^{37,38} This levelling of the ΔH_j° values is brought about by a combination of several causes.³⁸ Firstly, the heat of solvation of the mercury(II) ion is considerably larger in DMSO than in water,³⁶ which tends to decrease the values of $-\Delta H_j^\circ$, and preferentially for the first steps. Secondly, the differences between the heats of solvation of the halide ions are much smaller in

DMSO than in water.^{36,39} Evidently, it so happens that the sum of these changes rather nicely counterbalances the change of ΔH_j° due to the switch from digonal to tetrahedral coordination. The switch will therefore not be marked by any drastic change of ΔH_j° . The values of ΔS_j° found in DMSO are, on the other hand, very informative.³⁸ For all the halide systems, extremely large positive values of ΔS_j° clearly show that a very extensive desolvation takes place when the first complex is formed. Smaller, though still quite large values of ΔS_j° indicate a less extensive, though still quite substantial desolvation in the second step. The values of ΔS_j° are quite small which means that already the HgX_2 complexes are relatively weakly solvated. This has also been confirmed by a determination of their heats of solvation which are indeed low compared to those of the presumably tetrahedral solvated CdX_2 and ZnX_2 molecules.³⁶

In analogy with the mercury(II) ion, the cadmium ion finally forms four-coordinated halide complexes CdX_4^{2-} in DMSO as the ligand ion concentration is increased.⁴⁰ The same is most probably true also in water, although in this solvent the chloride complexes are fairly unstable.⁴¹⁻⁴³ The complex CdI_4^{2-} has been found by X-ray diffraction measurements to be a regular tetrahedron in both solvents.^{44,45} There is every reason to believe that CdBr_4^{2-} and CdCl_4^{2-} have the same structure.

Also in analogy with Hg(II), both DMSO and aqueous solutions of Cd(II) and Zn(II) perchlorates very probably contain hexacoordinated metal ions solvates. This is strongly indicated already by the existence of the crystalline solvates $[\text{M}(\text{DMSO})_6](\text{ClO}_4)_2$,⁴⁶ and $[\text{M}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$,⁴⁷ where $\text{M} = \text{Zn}$ or Cd . Several crystal structure determinations⁴⁸⁻⁵² confirm the existence of discrete octahedrally coordinated solvate cations. By means of X-ray diffraction measurements,^{44,53} the hexahydrates have been found to exist also in aqueous solution, while no such direct proof of the existence of the hexasolvates in DMSO has so far been produced.

Contrary to mercury(II), cadmium(II) does not form any linear complexes. Therefore, only a change from the initial octahedral coordination to the final tetrahedral one is to be expected as halide is added to a solution of a cadmium(II) hexasolvate. The thermodynamic functions of the consecutive formation reactions also indicate that the change mainly occurs at a certain step of the complex formation. This step is characterized by values of ΔH_j° and ΔS_j° which are abnormally positive relative to the values

of the neighbouring steps. The switch takes place at different steps in the two solvents, viz. at the formation of the third complex in water but at the formation of the second one in DMSO.⁴⁰

In the solids $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$, $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$, and $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$, the solvent molecules are coordinated *via* oxygen.^{32,46,48,54} For the very soft acceptor mercury(II), a coordination *via* the soft sulfur atom would perhaps rather have been expected. The most important reason why this does not occur is presumably that the donor properties of the sulfur atom are very considerably reduced by its bonding to the electronegative oxygen. Also sterically, the oxygen coordination is certainly much more favourable. Rather as expected, the infrared spectra also indicate^{46,55} that the hard acceptor zinc(II) is oxygen coordinated in the solids $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ and $\text{Zn}(\text{ClO}_4)_2 \cdot 5\text{DMSO}$. It might be presumed that, for all three acceptors, oxygen coordination prevails also in solution but this has so far not been proved.

A direct structure determination of the solvates formed by these acceptors in DMSO would evidently decide whether the solvation number and mode of coordination inferred are indeed correct. While the mercury(II) and cadmium perchlorates are sufficiently soluble to allow a determination of the solvate structure by means of X-ray diffraction, this is unfortunately not the case for the zinc perchlorate. The concentrations of the solutions in equilibrium with the solid hexasolvates are 0.93, 0.70 and 0.29 M, respectively, at room temperature. On the other hand, recent improvements in the evaluation technique has allowed a considerable refinement of the parameters determined earlier for the hydrated mercury(II) ion in solution.³³

In order to obtain further information about the nature and strength of the various acceptor to solvent bonds Raman spectra of the saturated solutions of the zinc, cadmium and mercury(II) perchlorates have been recorded. With the modern laser technique, all these solutions yield spectra of high resolution. The bands principally due to the M—O stretching modes are discerned in both solvents and, in DMSO, also bands due to the M—O bending vibrations. The solution spectra are compared to those obtained for solid hydrates and DMSO solvates. In order to facilitate the assignments, the infrared spectra of the solid solvates have also been recorded.

Table 1. Compositions of the DMSO solutions at 25 °C in mol l^{-1} . The linear absorption coefficient, μ , is calculated for $\text{MoK}\alpha$ -radiation.

Hg(II)	Cd(II)	ClO_4^-	DMSO	μ/cm^{-1}
—	0.685	1.370	13.33	7.2
0.932	—	1.864	13.00	26.8
0.434	—	0.868	13.55	15.0

EXPERIMENTAL

Preparation and analysis of solvates and solutions. The DMSO solutions investigated were prepared by dissolving DMSO solvates of the metal perchlorates in DMSO. The solvent had been purified as described earlier.⁴⁶ The water content, determined by Karl Fischer titration,⁵⁶ was <0.08 %. The composition of the solutions, checked by EDTA titration,⁵⁷ is given in Table 1. Their densities were determined pycnometrically.

The solvates $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ and $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$ were prepared as described previously.⁴⁶ The mercury(II) hexasolvate prepared previously⁴⁶ was, on the other hand, not pure and stable enough to meet the demands of the present investigations, or of the potentiometric and calorimetric measurements also in progress.^{36,38} Its mercury(II) content was generally somewhat too low and varied significantly between different preparations. Moreover, the compound, as well as the DMSO solutions prepared from it, decomposed appreciably in a few weeks even at ordinary temperature. In a few months, the solutions might even turn dark yellow, with a very sizable reduction of the mercury(II) concentration. Instant decomposition of the solid solvate also took place at a much lower temperature (Table 2) than for the pure $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$ that has now been prepared by another route.³² While the impure solvate decomposed violently immediately upon melting, the pure one survives its melting by $\approx 80^\circ\text{C}$. Remarkably enough, the melting point of the pure compound is only slightly higher than that of the impure one. By a modified method of preparation, described below, a pure tetrasolvate was first obtained. From a saturated DMSO solution of the tetrasolvate, the pure hexasolvate crystallized.³²

The solid solvates were analysed for metal and sulfur as described before.^{46,57} Especially for the mercury compounds, the results are very close to the theoretical values, Table 2. As mentioned, this was not the case for the mercury hexasolvate prepared previously, whose values have also been entered.

Melting and decomposition points were determined using a Büchi apparatus. Measured densities,

Table 2. The crystalline DMSO solvates.

Compound	M.p./°C	Dec.p./°C	Metal/%		Sulfur/%		$D_m/\text{g cm}^{-3}$	$D_x/\text{g cm}^{-3}$
			Calc.	Found	Calc.	Found		
$[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$	168–174	195–205	8.92	8.98	27.43	27.04	1.52(2)	1.54
$[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$	188–190	200–210	14.41	14.14	24.66	24.49	1.58(1)	1.60
$[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$	126–129	204–207	23.10	23.12	22.15	22.20	1.96(2)	1.99
$[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2^{46}$	125–128	125–128	23.10	22.57	22.15	22.05	—	—
$\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$	167–168	170–174	28.17	28.19	18.02	18.00	1.76(3)	1.82

D_m were obtained from the apparent loss of weight in benzene. They are compared to calculated densities, D_x , from unit cell dimensions found in the structure determinations.^{32,48,54} The unit cell for $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ was found to be trigonal with $a=b=20.818(1)$ and $c=12.659(2)$ Å, by X-ray diffraction methods.

Preparation of $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$. Mercury(II) perchlorate trihydrate⁴⁶ (0.01 mol) was dissolved in a minimum amount of methanol (100 ml). A few drops of concentrated perchloric acid had previously been added to the methanol in order to minimize the hydrolysis of mercury(II). Still it was sometimes necessary to decant the solution in order to remove a slight solid residue. About 0.06 mol DMSO was then added and the solution cooled to about -78°C . Very small white crystals precipitated which were filtered in dry air at the low temperature and then dried in vacuum over silica gel at room temperature, in order to remove the methanol. This resulted in a recrystallization of the phase obtained originally into the tetrasolvate. Larger crystals, suitable for investigation by single X-ray diffraction technique,⁵⁴ were obtained by recrystallization at lower temperature, $\sim 5^\circ\text{C}$. The compound seems to be stable for years when stored over silica gel at room temperature.

Warning. Metal perchlorates and nitrates solvated by DMSO are generally powerful explosives and under certain conditions a violent reaction is easily triggered.^{46,58,59} During one of the earlier attempts to prepare a mercury(II) solvate, the compound obtained at room temperature from a methanol solution exploded with extreme violence, after having been kept for about two weeks in a desiccator over sulfuric acid. The explosion seemingly occurred without outer provocation. On the other hand, the solvates described above explode only when subjected to very unkind mechanical treatment and stand fairly high temperatures before a rapid decomposition occurs, Table 2. Generally, the sensitivity seems to decrease with increasing purity. This does not exclude that even pure DMSO solvates might be very explosive as is no doubt the case⁴⁶ with $\text{Ag}(\text{ClO}_4)_2 \cdot 2\text{DMSO}$.

Great caution must also be exercised when handling DMSO solutions of poisonous substances, such as mercury and cadmium salts, since these are easily carried through the skin by the DMSO which penetrates lipid tissues at an astonishing rate.⁵⁹ DMSO dissolves many natural and synthetic polymers.⁵⁹ The unusual solvent properties must of course be taken into account in the design of the apparatus, and also in order to ensure good personal protection.

X-RAY DATA

Data collection

The X-ray scattering of $\text{MoK}\alpha$ -radiation ($\lambda=0.71069$ Å) was measured from the free surface of the DMSO solutions, as described in previous papers.^{33,60} The solutions were enclosed in an airtight shield, with a cylindrical beryllium window for the X-rays. The scattered intensity was repeatedly measured at discrete points between the θ values 1.5 and 70° , where 2θ is the scattering angle. Intervals of 0.1° for $1.5^\circ < \theta < 15^\circ$ and 0.25° for $15^\circ < \theta < 70^\circ$ were used. At least 100 000 counts were accumulated for each point which corresponds to a statistical error of about 0.3%. All measurements were performed at $25 \pm 1^\circ\text{C}$.

Data reduction and corrections

All calculations were carried out by means of the KURVLR and PUTSLR programs.⁶¹ The measured intensities were corrected for background, polarization, and double scattering, and normalized to a stoichiometric unit of volume, V , corresponding to the average volume per metal atom in the solutions. The normalization was done by comparing the high angle region of the corrected intensities to the calculated sum of the independent coherent scattering and the fraction of the incoherent scattering reaching the counter. The correction for double scattering did not exceed 3% for any of the

three DMSO solutions. A few points clearly outside estimated statistical error limits were removed.

Only the low-absorbing cadmium solution (Table 1) had to be corrected for absorption effects.⁶² The largest correction of the intensity curve (at $\theta = 45^\circ$) was 3.3 %.

RHF scattering factors, f , for the neutral atoms^{63,64} were used, except for H, where the spherical form factors proposed by Stewart *et al.* were employed.⁶⁵ For the recalculation of the aqueous mercury(II) perchlorate solution A1 of Ref. 33, spherical form factors for the H_2O molecule were used.⁶⁶ Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were applied for all atoms.⁶⁴ The incoherent scattering factors, I_{incoh} , were taken from the same sources as before.⁶ Correction for the Breit-Dirac factor^{67,68} in the appropriate form for a radiation counter, $(\lambda/\lambda')^2$, were applied.⁶⁹

The reduced intensity curves, $i(s)$, were calculated for each experimental point from:

$$i_{\text{obs}}(s) = I_{\text{obs}}(s) - \sum_m \{ (f_m(s) + \Delta f_m')^2 + (\Delta f_m'')^2 + \text{del}(s) (\lambda/\lambda')^2 I_{m,\text{incoh}}(s) \}$$

Here $I_{\text{obs}}(s)$ are the corrected and normalized intensities and $s = 4\pi\lambda^{-1} \sin \theta$. The summations are performed over all the atoms m in a stoichiometric unit of volume, V . The function $\text{del}(s)$, describing the fraction of the incoherent radiation which passes the monochromator, was determined as follows. The apparent shape of the spectrum of the Mo-tube was measured after reflection by the (200) lattice planes in the LiF-monochromator used. For radiation scattered incoherently, the wavelength (in Å) is increased: $\lambda' = \lambda + 0.02426(1 - \cos 2\theta)$.⁶⁴ The relative intensity at the wavelength λ' from the measured spectrum compared to the peak intensity at $\lambda(K\alpha)$ then gives $\text{del}(s)$ for the scattering angle 2θ .

An independent check of this function at high angles ($2\theta > 135^\circ$) was obtained by measurements with a Zr-filter.⁷⁰

The electronic radial distribution functions, $D(r)$, were calculated as $D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{s_{\text{max}}} s i(s) \times \text{Mod}(s) \sin(rs) ds$ where the modification function, $\text{Mod}(s)$, was $\{f_m^2(0)/f_m^2(s)\} \exp(-0.01s^2)$, ($M = \text{Cd}$ or Hg) and $\rho_0 = \{(\sum_m (f_m + \Delta f_m')^2 + (\sum_m \Delta f_m'')^2)/V\}$.

Finally, a correction was made for errors giving low-frequency additions to the $i(s)$ curves. Small spurious peaks below 1 Å in the $D(r)$ functions, which could not be related to interatomic distances, were removed by a Fourier transformation procedure.⁷⁰

The calculations of intramolecular intensity contributions and peak shapes were carried out as described previously.^{6,61}

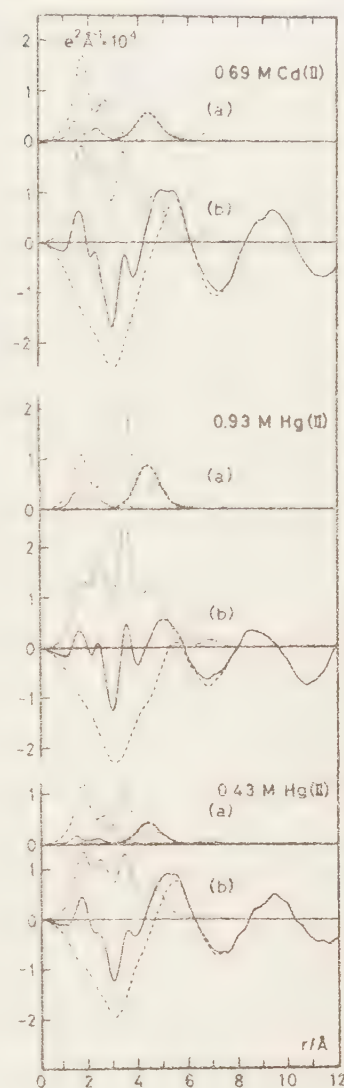


Fig. 1. (a) Peak shapes calculated for the refined models of the DMSO solutions, using the parameter values in Table 3, columns B. Dotted lines refer to M-O, M-S, S-S and O-O interactions, solid lines with large dots to M-C interactions within the complex $[\text{M}(\text{DMSO})_6]^{2+}$. Dashed lines refer to S-O, S-C, O-C and C-C interactions within DMSO, and solid lines to Cl-O and O-O interactions within ClO_4^- . (b) $D(r) - 4\pi r^2 \rho_0$ functions (solid lines) compared with sums of calculated peak shapes (dotted lines). The differences are shown by the dashed lines.

Results

Intensity curves and radial distribution functions (RDF). The experimental distribution functions, $D(r) - 4\pi r^2 \rho_0$, are shown in Fig. 1. The peaks found at about 2.3 and 3.4 Å in the RDF's fit in with the M—O and M—S distances expected for an octahedral complex and are close to corresponding values found in the crystal structures of the hexa-solvates.^{12,48}

Intramolecular DMSO-distances should occur at about 1.52 (S—O), 1.78 (S—C) and 2.7 Å (O—C and C—C).^{10,32,48,71,72} The S—O and S—C interactions explain the observed peak at 1.6–1.7 Å (Fig. 1). Expected Cl—O and O—O distances within the tetrahedral ClO_4^- ion are 1.43 and 2.33 Å, respectively.⁷³ Two broad peaks at about 5–6 and 9–10 Å also occur in the RDF's. They are, as well as the sharp intensity peak at $s \sim 1.5 \text{ Å}^{-1}$ (Fig. 2), features also found in an X-ray diffraction study of liquid DMSO,^{2a} and are very probably mainly

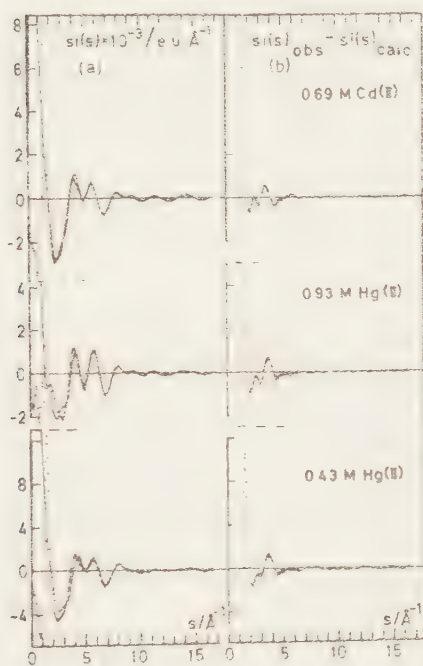


Fig. 2. (a) Reduced intensities multiplied by s for the DMSO solutions investigated. Experimental values are denoted by dots, values calculated for the refined model (with the parameter values in Table 3, column B) by solid lines. (b) Differences between experimental and calculated values.

caused by intermolecular interactions between DMSO molecules.

For the 0.93 M mercury(II) perchlorate solution, a separation of the intensity contributions from the various interactions can be performed with fair accuracy. This has been done in Fig. 3, where the functions $si(s)$ have been plotted separately for the various types of intramolecular interaction taking place in the solution, viz. those due to the complex formation, and those originating from the DMSO molecules and the perchlorate ions. The interactions due to the complex formation have been further divided so that the contributions from Hg—O, Hg—S, O—O and S—S have been combined, while the contribution from Hg—C has been separated.

For all three solutions investigated, the sum of

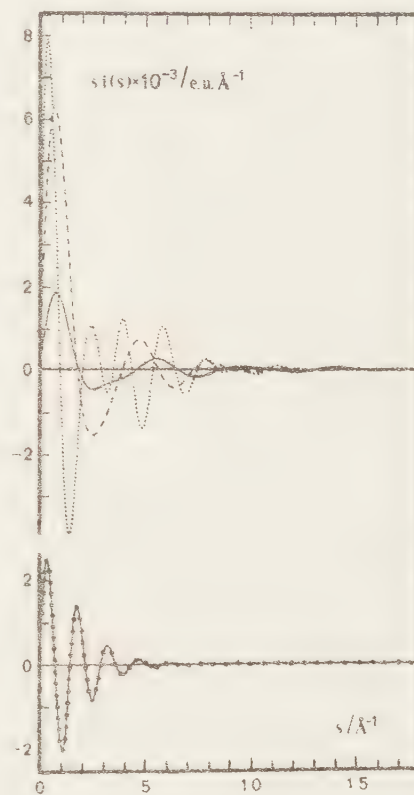


Fig. 3. Separation of the reduced intensities between various interactions for 0.93 M mercury(II) perchlorate in DMSO. The various lines refer to the same interactions as in Fig. 1a. For clarity, the highly damped curve of the Hg—C interactions is shown separately in the lower part of the figure.

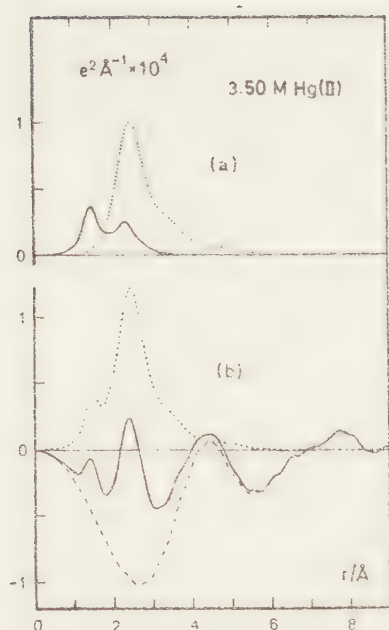


Fig. 4. (a) Peak shapes calculated for intramolecular interactions within the $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$ complex (dotted line) and the ClO_4^- ion (solid line), using the parameter values in Table 4, column B. (b) $D(r) - 4\pi r^2 \rho_0$ function for the acidic aqueous 3.50 M $\text{Hg}(\text{ClO}_4)_2$ solution (solid line), the sum of the calculated peak shapes (dotted line), and the difference between them (dashed line).

all the calculated intramolecular reduced intensity contributions, $i_{\text{calc}}(s)$, are compared with the experimental $i_{\text{obs}}(s)$ curves of Fig. 2a, after multiplication by s . As can be seen from the differences $si_{\text{obs}} - si_{\text{calc}}$ in Fig. 2b, these intramolecular intensities are the dominant contributors to the high angle regions of the observed intensity curves, where the effect of the highly damped intermolecular contributions become negligible.⁶

A recalculation of the aqueous mercury(II) perchlorate solution A1 in Ref. 33 (3.50 M $\text{Hg}(\text{ClO}_4)_2$ + 0.64 M HClO_4) was performed, since it was felt that, with the better scattering factors now available and the efficient data treatment now possible,⁶¹ a more precise value of the Hg–O bond length could be obtained, to be compared with the present data. The $D(r) - 4\pi r^2 \rho_0$ curve obtained is shown in Fig. 4. Distinct peaks are found at 1.4 and 2.4 Å. The shorter distance can be identified with Cl–O

in the perchlorate ion⁷³ and the longer one with Hg–O in the hydrated Hg^{2+} ion.³¹ A contribution to the peak at 2.4 Å also comes from the O–O interactions in ClO_4^- . These assignments are founded on the distances determined in crystal structures. The broad peak at about 4.5 Å is mainly caused by intermolecular interactions in the solutions as is discussed later.

Least-squares refinements. The parameter values of the models used for calculations of intramolecular intensity contributions can be refined using the high angle regions of the intensity curves. A series of refinements were performed where a minimum was sought^{6,61} for the weighted error-square-sum $\sum_{s_{\text{min}}}^{s_{\text{max}}} w(s) \{i_{\text{obs}}(s) - i_{\text{calc}}(s)\}^2$. The weighting function, $w(s)$, was proportional to $I_{\text{obs}}^{-2} \cos \theta$, which gives each part of the refined $i(s)$ curve a weight corresponding approximately to its statistical precision and also compensates for the unequal spacing between the points caused by the constant $\Delta\theta$ interval used during the intensity measurements.

To check for correlations between the parameters of the refined models, different combinations of parameters were refined. Those held constant were systematically given different values within their probable limits of variation.⁷⁴ The influence of systematic errors in different parts of the intensity curves were estimated by using different s ranges in the refinements. Especially the lower s limit was varied.⁶

For the DMSO solutions, the model selected in the final refinements consisted of the following parts.

1. Oxygen coordinated $\text{M}(\text{DMSO})_6^{2+}$ complexes, where the distances d of the M–O and M–S interactions, the coefficients b of their temperature factors $\exp(-bs^2)$ and, in some cases, the number of distances, n , were refined. The contributions from the O–O and S–S interactions, assuming octahedral arrangements around the metal atoms as in the crystal structure of $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$,³² were also introduced.

2. Pyramidal DMSO molecules, where in some cases the S–O and S–C distances and a b value, common to S–O and S–C, were refined. The O–C and C–C distances were taken from the crystal structure of pure DMSO at 5 °C.⁷¹ The b values of these interactions were assumed to be twice as large as the refined one for the S–O and S–C interactions. The C–H distance 1.08 Å and $b_{\text{C-H}} = 0.0030 \text{ Å}^2$ were used.⁷⁵ All DMSO molecules,

Table 3. Results of the least-squares refinements of the DMSO solutions. The refined parameters, d = distance (Å), b = temperature factor coefficient (Å²) and n = number of distances per metal atom, are obtained for the range $6 < s < 16$ Å⁻¹ of the reduced intensity curves. Estimated standard deviations are given within parentheses for refined parameters. In columns *A* all parameters in the table have been independently refined, in columns *B* a few are held constant.

Complex	Interaction	Parameter	0.69 M Cd(ClO ₄) ₂ <i>A</i>	0.93 M Hg(ClO ₄) ₂ <i>B</i>	0.93 M Hg(ClO ₄) ₂ <i>A</i>	0.93 M Hg(ClO ₄) ₂ <i>B</i>	0.44 M Hg(ClO ₄) ₂ <i>B</i>
M(DMSO) _n ²⁺	M—O	d	2.290(3)	2.294(2)	2.394(3)	2.392(3)	2.39(1)
		b	0.0041(5)	0.0044(3)	0.010(1)	0.0098(3)	0.013(1)
	M—S	d	3.417(3)	3.422(3)	3.426(3)	3.427(3)	3.437(5)
		b	0.016(1)	0.0154(4)	0.018(1)	0.0190(3)	0.016(1)
	M—O and M—S	n	6.5(4)	6	5.6(2)	6	6
ClO ₄ ⁻ DMSO	Cl—O	d	1.425(3)	1.426	1.447(5)	1.426	1.426
	S—O	d	1.559(3)	1.53	1.51(1)	1.53	1.53
	S—C	d	1.814(3)	1.80	1.78(1)	1.80	1.80
		b	0.0032(2)	0.0031(2)	0.0036(3)	0.0036(2)	0.0034(4)

Table 4. Results of least-squares refinements of an aqueous 3.5 M Hg(ClO₄)₂ solution in 0.64 M HClO₄. The refined parameters with the estimated standard deviation within parentheses are obtained for the range $4 < s < 16$ Å⁻¹ of the reduced intensity curve. In column *A* only Hg—H₂O and Cl—O interactions are taken into account, while in column *B* also H₂O—H₂O interactions along the edges of a regular octahedron are included. Spherical formfactors are used for the water molecules.⁶⁶

Complex	Interaction	Parameter	<i>A</i>	<i>B</i>
Hg(H ₂ O) _n ²⁺	Hg—H ₂ O	d	2.40(1)	2.41(1)
		b	0.022(3)	0.026(1)
		n	5.4(4)	6.0(4)
	H ₂ O—H ₂ O	d		$2.41 \times \sqrt{2}$
		b		0.022(7)
		n		12
ClO ₄ ⁻	Cl—O	d	1.423(4)	1.420(4)

bonded or non-bonded, were accounted for in this way.

3. Regular tetrahedral ClO₄⁻ ions, for which only one parameter, determining all distances, was independently refined. The b values were taken from mean-square amplitudes of vibration calculated from spectroscopic data.⁷⁶ The values $b_{\text{Cl—O}} = 0.00074$ and $b_{\text{O—O}} = 0.0016$ Å² were used.

For the aqueous solution the model used in the final refinements was the hydrated Hg(II) ion, where the three parameters d , b and n , describing the Hg—H₂O interactions, were refined. H₂O—H₂O interactions, assuming octahedral coordination around mercury, were introduced. A regular ClO₄⁻ tetrahedron was included as described above.

The parameter values of the DMSO solutions, from refinements in the range $6 < s < 16$ Å⁻¹, are

summarized in Table 3, and the ones of the aqueous solution, in the range $4 < s < 16$ Å⁻¹, in Table 4. Significant deviations occurred in the values when the lower s limit was ≤ 5 for DMSO and ≤ 3 for water. This is also indicated by the differences between experimental and calculated $si(s)$ curves for the DMSO solutions in Fig. 2b.

The standard deviations given in Tables 3 and 4 are those calculated in the least-squares process. From the variation of the results with different ranges of s , it seems that the inherent systematic errors may be of the same order of magnitude and the estimated standard deviations given in the text have been accordingly increased to give a more realistic error estimate.⁷⁴

Discussion

The solvated Cd^{2+} and Hg^{2+} ions in DMSO. If assumed to be the same, the number of M—O and M—S distances obtained in the least-squares refinements (columns A in Table 3) is six, within the estimated limits of error. Also when the number is allowed to vary independently for the two interactions, the same result emerges, though the error becomes larger. This of course further confirms that the lower peaks at 2.3 Å are due to M—O and the higher ones at 3.4 Å to M—S interactions, i.e. that both Cd^{2+} and Hg^{2+} are in fact coordinated *via* oxygen.

When the constant contributions from O—O and S—S interactions within the same complex, assuming octahedral configurations, were included in the refinements, the error-square-sum decreased 3–4%. A coefficient b corresponds to a root-mean-square variation, $l = \sqrt{2b}$, in the average distance. This l value includes both mean-square amplitudes from thermal vibrations⁷⁵ and more permanent variations of the distance for a specific type of interaction. The $b_{\text{S-S}}$ was therefore given a rather large value, 0.04 Å² ($l = 0.28$ Å), corresponding to the expected large variation in the individual S—S distances.^{32,48}

An inclusion in the refinements of the M—C interactions, which vary considerably around an average of 4.4 Å^{32,48} in the crystal structures did not reduce the error-square-sum for the refined high angle regions of the intensity curves ($s > 6$ Å⁻¹). This indicates that large variations in the M—C distances occur also in the solutions, corresponding to the estimated large b value ≈ 0.07 Å².

Especially for M—O, the number of distances, n , is strongly correlated to the b value. Therefore, calculations have also been performed with a constant coordination number of six. This results in more precise b values, but the other parameters do not change significantly, Table 3.

The $b_{\text{Cd-O}}$ value corresponds to $l = 0.085(4)$ Å. This is not much larger than the expected vibrational amplitude. The spread of the Cd—O distances is thus small, confirming that the coordination is regularly octahedral.

The $b_{\text{Hg-O}}$ is significantly larger, corresponding to $l = 0.15(1)$ Å. This probably does not reflect any permanent deviation from regular octahedral symmetry, however, since the Hg—O peak (Fig. 1) seems too symmetrical to contain Hg—O interactions from a markedly distorted octahedral con-

figuration. If any of the bonds were markedly shorter and stronger, they also ought to have small b values and therefore be prominent in the outermost parts of the intensity curves. No sign of such an influence has been detected, however.

Comparisons between the RDF's and the calculated peak shapes for the refined model (see above) using the parameter values in Table 3, columns B, are made in Fig. 1. The M—C interactions are also included, with the average distance 4.4 Å and the estimated $b_{\text{M-C}} = 0.07$ Å² ($l = 0.37$ Å). Smooth difference curves are obtained showing that the refined model accounts for all distinct intramolecular interactions.

The hydrated Hg^{2+} ion. Within the estimated limits of error six oxygen atoms are found to be coordinated to Hg (Table 4). The parameters obtained, when only the Hg—H₂O and the intramolecular interactions in ClO_4^- are taken into account, are listed in column A, Table 4. There is, however, a small shoulder at 3.4 Å in the RDF (Fig. 4) corresponding to O—O distances along the edges of a regular octahedral complex. Such expected O—O interactions were therefore included in the refinements, adjusting only the $b_{\text{O-O}}$ independently (column B, Table 4). The error-square-sum then decreased by 5%.

The b value of the Hg—O distances is rather large, corresponding to a root-mean-square variation $l = 0.23(1)$ Å. For the same reasons as discussed for $\text{Hg}(\text{DMSO})_6^{2+}$, however, the average symmetry seems to be regularly octahedral (cf. Fig. 5, Ref. 33). This is also supported by the relatively small average $l = 0.21(3)$ Å obtained for the non-bonded O—O distances along the octahedral edges.

Peak shapes, calculated from the parameter values in column B, Table 4, have been subtracted from the RDF of the aqueous solution. A smooth difference curve was obtained (Fig. 4), which supports the assumption of a regular octahedral coordination around mercury.

Comparison of the structures of the DMSO solvates of Hg^{2+} and Cd^{2+} in solution and in crystals. In the octahedrally oxygen coordinated solid compounds $[\text{M}(\text{DMSO})_6](\text{ClO}_4)_2$, the orientation of the DMSO ligands differ for Cd^{2+} and Hg^{2+} .⁴⁸ For the Cd complex even alternative orientations are found. In solution, the DMSO ligands certainly have a considerable freedom of movement. As the methyl groups have a rather large free volume available,^{32,48} rotations around the M—O and S—O bonds should be possible. This would give

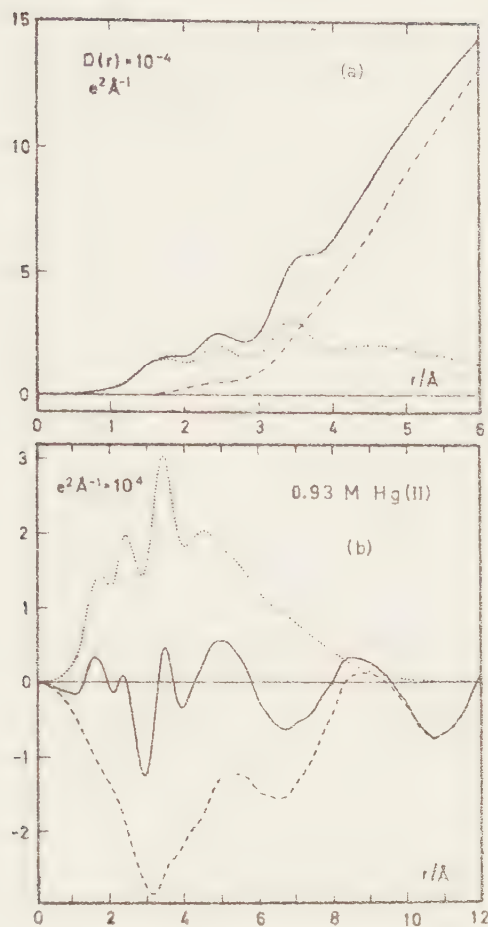


Fig. 5. (a) $D(r)$ curve (solid line) for the 0.93 M $\text{Hg}(\text{ClO}_4)_2$ solution in DMSO, compared with the sum of the calculated peak shapes (dotted line) for all intramolecular interactions within $[\text{Hg}(\text{DMSO})_6]^{2+}$, free DMSO and ClO_4^- . For $[\text{Hg}(\text{DMSO})_6]^{2+}$ the positional parameters from the crystal structure determination in Ref. 32 were used, except for the Hg–O distances which were lengthened to 2.393 Å. The dashed line gives the difference between the functions. (b) $D(r) - 4\pi r^2 \rho_0$ function (solid line), the sum of the calculated peaks (dotted line), and the difference between them (dashed line).

constant M–O and M–S, but varying M–C distances, as is in fact found. There are therefore no reasons to believe that the different shapes found in the crystals would persist in solution.

Discrete dinuclear complexes with a double DMSO oxygen bridge are found in the structure of $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$.⁵⁴ The Hg–Hg distance is 3.913(4) Å. Also in the structure of $3\text{HgCl}_2 \cdot 2\text{DMSO}$ such a double bridge exists. In this case, the Hg–Hg distance is 4.016 Å.¹⁰ Therefore, the RDF's were checked for signs of bridge-formation. No trace of such Hg–Hg distances could be found, however.

The complex $\text{Hg}(\text{DMSO})_6^{2+}$ in the crystals of $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$ has been used to calculate peak shapes for a comparison with the RDF of the 0.93 M $\text{Hg}(\text{ClO}_4)_2$ solution (Fig. 5). The positional parameters obtained in the structure determination were used,³² except for the Hg–O distance which was lengthened to 2.39 Å. The freedom of rotation of the DMSO ligands was accounted for by giving the appropriate interactions rather large b values. The intramolecular interactions of ClO_4^- and non-bonded DMSO were also included in the same way as described before. The main difference between this model and the previously refined one is that all intramolecular interactions within $\text{Hg}(\text{DMSO})_6^{2+}$ are now taken into account. Subtraction of peak shapes, calculated with this model, from the RDF's give smooth background curves with fairly low electron pair densities up to 4–5 Å (dashed curves in Fig. 5). This indicates that intermolecular interactions from the heavy metal atoms to the ClO_4^- ion and to free DMSO molecules are not frequently occurring within a radius of about 5 Å from the metal atoms. This is consistent with an approximately octahedral arrangement of the S atoms, just as in the solid compound. The remaining broad peaks at about 5.5 and 9 Å in the background curve, agree with peaks found for intermolecular interactions in liquid DMSO.² In the solution, non-coordinated DMSO molecules, as well as ClO_4^- ions, are evidently kept away from the mercury rather efficiently by the movements of the DMSO ligands attached to the mercury atoms.

Comparison of the structure of the hydrated Hg^{2+} in solution and in crystal. The very concentrated solution used, 3.5 M $\text{Hg}(\text{ClO}_4)_2$ in 0.64 M HClO_4 , contains less than five non-bonded H_2O molecules per $\text{Hg}(\text{H}_2\text{O})_6^{2+}$ complex. A comparison with intermolecular interactions involving Hg atoms in the structure of the solid hydrate, $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ is therefore of immediate interest. In this compound a slight deviation from a regular octahedral O_h symmetry for the $\text{Hg}(\text{H}_2\text{O})_6^{2+}$ complexes is observed.³¹ This is probably an effect of H-bonds between the complexes leading to Hg–Hg distances

of 5.34 Å. There are no indications of such Hg–Hg interactions in the RDF (Fig. 4), and H-bonds between the complexes are evidently not formed in the solution.

In the solid hydrate each Hg is surrounded by six equidistant ClO_4^- . There are therefore six Hg–Cl distances at 4.75 Å, 12 Hg–O distances at 4.39 Å, and another six at 4.64 Å. They correspond very well to the large and broad peak from about 4 to 5 Å which remains in the “back-ground” curve discussed above (dashed curve in Fig. 4). This strongly indicates that in this concentrated solution the complex $\text{Hg}(\text{H}_2\text{O})_6^{2+}$ is surrounded by ClO_4^- ions at much the same distance as in the solid (cf. the results of the refinements in Table 3, Ref. 33).

Bond lengths, bond angles and ionic radii. The Cd–O bond length 2.292(4) Å, found in DMSO solution of $\text{Cd}(\text{DMSO})_6^{2+}$, does not differ significantly from the well-defined Cd–O1 bond length, 2.278(7) [2.291]* Å, in the crystalline solvate $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$.⁴⁸ Also in aqueous solution, much the same bond lengths have been found, viz. 2.289 ± 0.013 and 2.31 ± 0.02 Å,^{53,44} and these are not significantly different from the average Cd–O bond length in the crystalline hydrate $[\text{Cd}(\text{H}_2\text{O})_6](\text{NH}_4)_2(\text{SO}_4)_2$, viz. 2.28 Å.⁴⁹

On the other hand, the average Hg–O bond length is significantly longer in the solutions studied than in the crystalline solvates. In aqueous and DMSO solutions (Tables 3 and 4) the values found are 2.41(1) and 2.393(5) Å, respectively, while 2.341(6) [2.349]* Å is found in $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and 2.338 [2.350]* Å in $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$.^{31,32}

In solution, the average values of the angle M–O–S are 120.2(1.0) and 125.7(1.0)° for the Hg and Cd solvates, respectively. This is not significantly different from the corresponding values 123 and 125° in the crystalline solvates.^{32,48}

Nor do the intramolecular S–O and S–C distances obtained in the refinements (Table 3) in the DMSO molecules in solution differ significantly from the values found in crystals of DMSO⁷¹ or oxygen coordinated solvates,^{32,48} see also surveys in Refs. 10 and 72.

The Cl–O bond length in ClO_4^- found in the least squares refinements agrees very well with that found in crystal structures, especially where only weak hydrogen bonding occurs.⁷³

From the average bond lengths obtained, the

ionic radii of Cd^{2+} and Hg^{2+} in octahedral coordination can be derived. If the radii of oxygen are taken as 1.35 Å in the two-coordination of the DMSO solvates and as 1.36 Å in the three-coordination of the hydrates,⁷⁷ virtually the same radii, $r(\text{Cd}^{2+}) = 0.94$ Å and $r(\text{Hg}^{2+}) = 1.05$ Å, are found for both DMSO and aqueous solutions. From the crystalline DMSO solvates, $r(\text{Cd}^{2+}) = 0.92$ Å and $r(\text{Hg}^{2+}) = 0.99$ Å are calculated, from the hydrates 0.92 Å and 0.98 Å. The radii found for the solids are thus somewhat shorter than found for the solutions, and in the case of Hg^{2+} the difference is certainly significant. The radii derived from crystal structures by Shannon and Prewitt⁷⁷ are somewhat longer than the present ones, however, viz. $r(\text{Cd}^{2+}) = 0.95$ Å and $r(\text{Hg}^{2+}) = 1.02$ Å, i.e. rather close to the values presently found in solution.

While the octahedral bond length relative to oxygen is ≈ 0.1 Å longer for Hg(II) than for Cd(II), the bond lengths do not differ significantly in the tetrahedral tetraiodo complexes. The Cd–I bonds are 2.79 Å both in DMSO⁴⁵ and in aqueous solution⁴⁴ and the Hg–I bonds are 2.80 and 2.785(3) Å, respectively.^{1,6} In the tetrachloro complexes, on the other hand, the bond length of Hg(II) seems again to be slightly longer than of Cd(II). Admittedly, only one reliable determination has so far been performed in solution, viz. for HgCl_4^{2-} in water,⁷ where the distance Hg–Cl is 2.47(1) Å. This result agrees well with those found for solids,^{26,25} viz. 2.46₄ and 2.50 Å. Thus, in the case of this complex, the distance seems to be the same in solution and in crystalline compounds. For CdCl_4^{2-} , the average distance Cd–Cl in two recently investigated solid compounds⁷⁸ is 2.45₄ Å, i.e. most probably shorter than the mean of the values found for Hg–Cl.

The bond distance Hg–L thus becomes shorter relative to Cd–L as the ligand atom L becomes softer, and the bonding hence more covalent, in the sequence $\text{O} < \text{Cl} < \text{I}$. As might be expected, the softer acceptor Hg^{2+} is able to utilize the covalent bonding capacities of the softer ligands more efficiently than Cd^{2+} , with the result that the bonds Hg–L are strengthened, and consequently also markedly shortened relative to the bonds Cd–L. For the very soft iodide ion, the effect becomes so considerable that the bond lengths, and hence the radii of Hg^{2+} and Cd^{2+} , become virtually equal. For even softer ligands, $r(\text{Hg}^{2+})$ might well be even shorter than $r(\text{Cd}^{2+})$. Such an inversion has in fact been observed between the neighbour acceptors

* Corrected for thermal motion assuming oxygen to ride on the metal atom.

gold(I) and silver(I). In the bidentate complexes MCl(PP) ,⁷⁹ the bonds $\text{Au}-\text{P}$ are 0.1 and 0.15 Å shorter than the corresponding bonds $\text{Ag}-\text{P}$ while $\text{Au}-\text{Cl}$ is 0.3 Å longer than $\text{Ag}-\text{Cl}$.

RAMAN AND INFRARED SPECTRA

Data collection

The Raman spectra were recorded in the range 1550 to 150 cm^{-1} , with a Cary 82 argon ion laser spectrophotometer using the 4880 Å line. Glass tubes of 1 mm diameter were used both for the solids and the solutions. The infrared spectra were recorded in the range 4000 to 230 cm^{-1} , with a

Perkin-Elmer 221 or a Beckman IR-9 spectrometer. In the low-frequency range, 400 to 150 cm^{-1} , the measurements were carried out on an RIIC FS-720 Fourier spectrometer at liquid nitrogen temperature. All other measurements were carried out at room temperature. Depending upon substance and frequency, various techniques had to be used (polyethylene or KRS-5 windows; KBr pellets).

Results and discussion

DMSO solvates of Zn^{2+} , Cd^{2+} and Hg^{2+} in solids and solutions. The Raman and infrared spectra recorded display a large number of bands. These can be divided into three distinct groups, viz. bands

Table 5. Raman bands (cm^{-1}) of pure DMSO(l), of solid solvates $[\text{M(DMSO)}_6](\text{ClO}_4)_2$, $\text{M} = \text{Zn, Cd, Hg}$ and $\text{Hg(ClO}_4)_2 \cdot 4\text{DMSO}$ ($= \text{Hg 4}$), and of the saturated DMSO solutions of the hexasolvates. Intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

DMSO(l)	Hexasolvates				Solutions ^a			Vibration
	Zn	Cd	Hg	Hg 4	Zn	Cd	Hg	
	~416 w 176 w	~412 w 197 m	422 m 221 m	~420 m	415 vw 175 vw	~411 vw 195 w	425 w 202 m	M-O str, sym M-O bend
1420 m	1425 vs	1425 s	1405 s			1422 s	1420 s	C-H def, asym
1310 w	1325 vw	1305 vw	1320 w			1312 w	1313 w	C-H def, sym
1045 vs	1042 m				1047 s	1047 s	1048 s	S-O str
	1021 s	1028 s	1028 s	1029 w			1025 m ^b	S-O str
997 vw	1003 m	1007 m	1001 m	998 w	1000 vw	1005 vw	996 vw	C-H rock
995 m	954 m	962 m	960 vw		955 m	955 w	950 ww	C-H rock
928 vw	912 m	912 m	909 m		912 w	912 w	911 w	C-H rock
	717 s	717 s	717 s	718 s		~712 m ^b	713 m ^b	C-S str, asym
699 s					698 m	700 m	700 m	C-S str, asym
	683 vs	681 vs	683 vs	683 vs				C-S str, sym
670 vs					668 vs	672 vs	674 vs	C-S str, sym
			399 m	402 m			397 w ^b	C-S-O def, sym
382 m					383 m	384 m	384 m	C-S-O def, sym
	345 s	343 s	342 s	341 s				C-S-O def, asym
332 s					334 s	338 s	336 s	C-S-O def, asym
	317 s	315 s	316 s	314 m				C-S-C def
308 m					308 m	311 m	310 m	C-S-C def
	1102 m	1100 m	1100 m	1093 m				Cl-O
	935 vs	932 vs	932 vs	932 s	932 s	933 s	933 s	Cl-O
	626 m	626 m	625 w	621 w	^c	625 w	626 w	Cl-O
	460 m	460 m	459 w	463 w	457 w	458 w	460 w	Cl-O

^a Concentrations: Zn, 0.29 M; Cd, 0.71 M; Hg, 0.93 M. ^b Shoulders. ^c Covered by the very strong C-S stretch at 668 cm^{-1} .

Table 6. Infrared bands (cm^{-1}) of pure DMSO(l), and of solid solvates $[\text{M}(\text{DMSO})]_6(\text{ClO}_4)_2$, $\text{M} = \text{Zn}$, Cd , Hg , and $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ ($= \text{Hg } 4$).

DMSO(l)	Hexasolvates				Vibration
	Zn	Cd	Hg	Hg 4	
	431 m 192, 178 w	418 m 191, 195 w	445 s		M—O str, asym M—O bend
2985 s	2978 vw	2970 vw	2980 vw	2985 vw	C—H str
2902 s	2900 vw	2899 vw	2900 vw	2900 vw	C—H str
1432 s		1418 m	1425 vw	1429 w	C—H def, asym
1401 s	1412 vw	1395 m	1397 vw	1397 w	C—H def, asym
1305 m	1303 vw	1304 w		1305 w	C—H def, sym
1048 vs	1015 m	1019 m	1025 m	1015 s	S—O stretch
949 m	948 m	947 m	948 m	945 s	C—H rock
690 m	694 w	695 w	692 w	697 w	C—S stretch, asym
660 w	660 vw	665 vw	666 vw	665 vw	C—S stretch, sym
378 m	368 w	370 w	370 w	371 m	C—S—O def, sym
327 m	321 w	320 w	322 w	340 m	C—S—O def, asym
	1100 w 621 vs	1088 m 621 vs	1100 w 621 vw	1088 s 621 vw	Cl—O Cl—O

due to the coordinate bond, to the bonds within DMSO, and to the bonds within ClO_4^- .

The well-known frequencies⁸⁰ of the Cl—O bands are, as expected, not shifted in the present solids or solutions, Tables 5 and 6.

On the other hand, the frequencies found in pure DMSO⁸¹ are shifted considerably when the solvent molecules are coordinated to a metal atom. As might be expected, the shifts are larger, the closer the bond associated with the vibration is to the site of coordination. As will be further discussed below, the direction of the shifts depends upon whether the metal ion is coordinated *via* oxygen or *via* sulfur. Especially the S—O stretching frequency, strongly active in both Raman and infrared, exhibits very characteristic shifts. Those found in the infrared spectra have repeatedly been used to discern between different modes of coordination in solid solvates.^{82–85,46}

In addition to the ClO_4^- and DMSO bands, the solvates display two new bands of low energy, with wavenumbers just above 400 cm^{-1} and just below 200 cm^{-1} , Tables 5 and 6. The bands observed are of weak to medium intensity. The higher frequency band has been found earlier⁵⁵ in the infrared spectra of DMSO hexasolvates of several divalent metal ions, including Zn^{2+} . It has been assigned to the M—O stretching mode.⁵⁵ It seems natural to assign the band of lower frequency now discovered to

M—O bending modes. Evidence supporting this assignment will be presented below.

A coordination of a metal ion to the O-atom in DMSO should bring about a lowering of the S—O bond order and hence a decrease of the S—O stretching frequency relative to free DMSO. Conversely, a coordination to the S-atom should bring about an increase of the S—O bond order, and hence of the S—O stretching frequency.^{83,84} These inferences have later been amply confirmed by complete structure determinations of several of those solids which were used in the previous studies of infrared spectra.^{32,48,72,86}

The present Raman spectra of the solid hexasolvates show, as expected, shifts in the S—O stretching frequency very similar to those found in the infrared spectra, Table 5. The latter have moreover been checked, Table 6, with results that agree very well with those previously found.⁴⁶ The wavenumbers found in the pure solvent, 1045 cm^{-1} in Raman and 1048 cm^{-1} in infrared, are in all the solvates lowered by 20 to 30 cm^{-1} as expected for O-coordination. The same applies to the actually dimeric⁵⁴ $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$.

In solutions of these solvates, free DMSO predominates over coordinated DMSO, even if the solutions are saturated. It might be hoped, however, that the bands due to free and coordinated DMSO are resolved in the laser Raman spectra. Unfortun-

nately, the shifts are not large enough for such a resolution. Especially for Zn^{2+} , but also for Cd^{2+} , the solubility is so low that the bands due to coordinated DMSO only appear as rather insignificant shoulders on the low frequency side of the intense band due to free DMSO. For Hg^{2+} , however, where the solubility is higher, a well-developed shoulder is observed, consistent with a downward shift of the S—O stretching band in coordinated DMSO to $\approx 1025\text{ cm}^{-1}$, i.e. to the value found for the solid hexasolvate, Table 5. This is of course in line with the result of the structure determination reported above for $\text{Hg}(\text{DMSO})_6^{2+}$ in solution.

The decrease of the S—O bond order brought about by a coordination of a metal ion via the O atom should induce a compensatory increase in the C—S bond order. Consequently the wavenumbers of the C—S stretching modes, both the symmetric and the antisymmetric ones, should increase. Such shifts, ranging from 10 to 30 cm^{-1} , have in fact been observed in infrared for the antisymmetric mode.^{84,85} For the solvates studied here, corresponding shifts have been found for both modes, though smaller, only $\approx 5\text{ cm}^{-1}$, Table 6. Especially the bands due to the symmetric vibrations are of low intensity, however, so the determinations are not very precise. For the pure solvent, these bands are found at 660 and 690 cm^{-1} for the symmetric and antisymmetric mode, respectively. The values agree very well with those originally found by Cotton *et al.*⁸² and differ only slightly from later determinations which generally record wavenumbers $\approx 10\text{ cm}^{-1}$ higher.^{84,85} Also in the present Raman measurements, somewhat higher wavenumbers are found for these vibrations, viz. 670 and 699 cm^{-1} , in accord with earlier determinations,⁸¹ Table 5. For the solid solvates, upward shifts are again found, somewhat larger than in infrared, viz. 10 to 13 cm^{-1} for the symmetric and 16 to 17 cm^{-1} for the antisymmetric mode, Table 5. Most probably, the differences found between the infrared and Raman shifts are mainly due to the relatively low precision of the infrared measurements. There is no doubt, however, that the wavenumbers of the C—S stretching modes increase on the coordination of a metal ion to the O-atom, just as expected.

In saturated solutions of the mercury and cadmium solvates, these shifts appear as shoulders on the high frequency side of the bands due to free DMSO. The shoulders are especially marked for the bands due to the antisymmetric stretching,

where the shifts are larger. For the less soluble zinc solvate, on the other hand, the concentration of coordinated DMSO is too low to bring about any perceptible shoulders of the DMSO bands.

In contrast to earlier work,⁵⁵ we have found that also other vibrations involving the C—S bond, viz. the symmetric C—S—C deformation, and the symmetric and antisymmetric C—S—O deformations, increase their wavenumbers perceptibly in the solid solvates, Table 5. This is borne out beyond doubt by the Raman spectrum of the mercury(II) hexasolvate where all three modes are represented by bands of medium to strong intensity. For zinc and cadmium, the symmetric C—S—O bands presumably overlap with the M—O stretching bands which would imply upward shifts of $\approx 30\text{ cm}^{-1}$. Considering that shifts of more than 40 cm^{-1} have been found for lanthanide DMSO solvates,⁸⁷ this seems quite plausible. Moreover, at least the cadmium band has a deformed shape indicating a composite absorption.

Generally, the complex formation does not bring about large shifts of the vibrations involving the C—H bonds, Tables 5 and 6. Evidently, these are too far from the site of coordination to be much affected by the new bond. The C—H rocking band at 928 cm^{-1} has moved markedly downwards, however. Virtually the same shift is observed when liquid DMSO is vaporized, or diluted by carbon tetrachloride.^{81b} Most likely, therefore, this shift is due to the disappearance of the molecular packing preferred by the pure solvent.

Not surprisingly, the most direct information about the M—O coordinate bonds is provided by their own vibrations. The antisymmetrical stretching modes are displayed by the infrared spectra of the solid hexasolvates, Table 6. For zinc, the band is in exactly the same position as found in an earlier study.⁵⁵ In the Raman spectra, bands assigned to the symmetrical M—O stretching modes are found for all the hexasolvates, Table 5. For zinc and cadmium, the intensities are fairly low while the mercury band is well-developed. The frequencies are markedly lower than for the anti-symmetric stretching bands recorded in infrared. As the Raman data are more complete, and certainly are more precise, they will serve as the main basis for the following discussion.

Also the Raman spectra of the saturated solutions yield both the M—O bending and the M—O stretching bands, Table 5. In the case of zinc and cadmium, however, the concentrations are so low

that the bands are barely perceptible. For mercury they are stronger and, for some unknown reason, the wavenumber of the bending mode is lower than for the solid solvate.

The wavenumber of the stretching modes decreases from zinc to cadmium and then increases again the mercury, Tables 5 and 6. The latter value is even higher than that of zinc. This certainly holds even if, as postulated above, the zinc and cadmium bands in the Raman spectra are somewhat affected by the overlap with the C—S—O deformation frequency. For regularly octahedral complexes like the present ones, the stretching force constants are approximately proportional to the square of the wavenumbers for a symmetric stretching (*cf.* below) which means that they vary in a similar manner, with a marked minimum at cadmium, Table 8. The force constants of course do not measure the total strength of the M—O bonds but rather their resistance to a small disturbance.⁸⁸ Nevertheless, the minimum indicates that the Cd—O bond is most probably weaker than both Zn—O and Hg—O. The conclusion is moreover convincingly vindicated by the similar trend found for the heats of solvation, as will be further discussed below. The reason for the remarkable minimum of bond strength at Cd^{2+} must be the rapid change of bond character along the series Zn^{2+} , Cd^{2+} , Hg^{2+} . The small and hard acceptor Zn^{2+} forms a strong bond of a markedly electrostatic character. The very soft and much larger acceptor Hg^{2+} forms a strong bond of a rather covalent character. The intermediate Cd^{2+} is evidently handicapped by being on one hand much larger than Zn^{2+} , on the other much less soft than Hg^{2+} . The outcome is a bond of a lower overall strength than developed by either Zn^{2+} or Hg^{2+} .

This topic will be further discussed later on when the comparison can be extended to stretching force constants for bonds in other complexes of the three metal ions considered, and also to quantities connected with the total strength of these bonds.

The wavenumber of the vibration assigned to the M—O bending mode increases monotonously from zinc to mercury, Table 5. The resistance to this deformation thus increases as the bond becomes more covalent, and hence the directional forces stronger. This is evidently just what to expect for a bending mode and strongly confirms the assignment done for this vibration.

Hydrates of Zn^{2+} , Cd^{2+} and Hg^{2+} in solids and solutions. In the spectral studies of the hydrates, the interest has been focussed on the M—O bonds. In Raman, the symmetric stretching frequencies are found for all the solid solvates, and also for all the saturated solutions, Table 7. The wavenumbers are throughout lower than in DMSO. As in DMSO, a minimum is found at cadmium. In water, the wavenumber for mercury is lower than for zinc, however. The implications of these differences will be discussed below.

The wavenumbers found agree fairly well with those reported previously^{89,90} for near-saturated aqueous nitrate and perchlorate solutions (385–390 cm^{-1} for zinc, *ca.* 356 cm^{-1} for cadmium and 380 cm^{-1} for mercury).

For the solid hydrates, faint bands presumably due to the M—O bending mode are observed at $\approx 175 \text{ cm}^{-1}$. These bands are too poorly developed, however, to allow a reliable determination of the shifts between the various hydrates.

Force constants and bond strengths. For the present octahedral solvates, a valence force field approach allows a simple calculation of the primary

Table 7. Raman bands (cm^{-1}) of the solid hydrates $[\text{M}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, M=Zn, Cd, Hg, and of their saturated aqueous solutions.^a

Solvates			Solutions ^b			
Zn	Cd	Hg	Zn	Cd	Hg	Vibration
385 w	352 m	360 s	$\sim 380 \text{ m}$	352 m	370 m	M—O stretch
933 vs	933 vs	933 vs	933 s	933 s	933 s	Cl—O
631 s	630 s	627 s	630 m	627 m	629 m	Cl—O
463 s	465 s	466 s	464 m	461 m	462 m	Cl—O

^a No measurements at wavenumber $> 1000 \text{ cm}^{-1}$. ^b Concentrations: Zn, 3.26 M; Cd, 3.23 M; Hg, 3.50 M (+0.64 M HClO_4).

stretching force constants F_r . If it is assumed that the frequency is determined solely by the interaction between the metal ion and the oxygen ligand atom and if the secondary interaction constants are neglected, the following relation holds for the symmetric mode⁹¹

$$F_r = 4\pi^2 c^2 \bar{\nu}^2 N^{-1} A_L$$

where c = the velocity of light, $\bar{\nu}$ = the wavenumber, N = the Avogadro number and A_L = the atomic weight of the ligand atom.

Especially for the DMSO solvates, this approach is a considerable simplification of the actual conditions, as the vibrations of the ligand atom are influenced by the bond joining it to the rest of the DMSO molecule. The values of F_r calculated in this manner, listed in Table 8, will evidently represent the lower limits of the force constants in the present approximation. The other extreme, viz. insertion of the total mass of DMSO, would certainly yield values of F_r much further from the truth. However, the influence of the mixing with the bending modes is probably larger for the DMSO solvates than for the hydrates and would counteract the effect of a too small effective ligand mass in the calculations.

This is also borne out by a comparison with the corresponding values of F_r found for the hydrates (Table 8), where insertion of the mass of the whole ligand H_2O certainly is the best approximation. The values of F_r found are not very different from the lower limits calculated for the DMSO solvates. As there is no reason to believe, that the M—O bond strength differs radically between the hydrates and the DMSO solvates, the true values of F_r for the DMSO solvates should be fairly close to those calculated by insertion of the mass of the oxygen atom. Even when this minimum mass is applied, the values for the DMSO solvates are higher, and the M—O bonds, therefore, presumably stronger than for the hydrates. Comparisons between complexes of different acceptors with the same ligand are of course not influenced by this uncertainty.

It is also of interest to compare stretching force constants of these solvates with those found for other complexes of the acceptors studied. As to the gaseous linear^{3,92,93} halides MX_2 , the symmetric stretching frequencies are so far known only in the case of mercury. The antisymmetric stretching frequencies are, on the other hand, known for all the

Table 8. Stretching force constants of the M—O bonds in solid hexasolvates and of the M—X bonds in gaseous dihalides (10^5 dyn cm^{-1}).

	M—O			M—X		
	H_2O^a	H_2O^b	DMSO ^a	Cl^-	Br^-	I^-
Zn^{2+}	1.40	1.57	1.63	2.67	2.33	1.77
Cd^{2+}	1.17	1.32	1.60	2.34 ^c	1.93	1.61
Hg^{2+}	1.22	1.38	1.68	2.63	2.25	1.85

^a Force constants calculated with A_L = atomic weight of oxygen atom. ^b with A_L = molecular weight of water.

^c Corrected value, calculated from ν_3 of Ref. 92.

halides. Again assuming that the secondary interaction constant is negligible, the primary stretching force constant F_r can be calculated from⁹⁴

$$F_r = 4\pi^2 c^2 \bar{\nu}^2 N^{-1} \frac{A_L}{1 + 2A_L A_M^{-1}}$$

where A_M = the atomic weight of the metal. The values of F_r thus found are listed in Table 8. For the mercury systems, they differ somewhat from the set published previously⁹² which was calculated as the mean between the values of F_r found from the symmetric and antisymmetric stretching frequencies. It seems better, however, to compare data calculated on the same basis. It is nevertheless reassuring that the values calculated from the symmetric and antisymmetric stretching frequencies do not differ very much.

For all the dihalides, the value of F_r displays that minimum at cadmium which has already been noticed for the solvates, coordinated via oxygen. The lower bond strength of Cd^{2+} relative to both Zn^{2+} and Hg^{2+} thus persists even if the character of the coordinating ligand varies greatly. Moreover, Hg^{2+} is favoured relative to Zn^{2+} by a typically soft ligand as I^- (and also by DMSO!) while the reverse is true for a typically hard ligand as H_2O . The ligands Cl^- and Br^- are intermediate, as might be expected.

The heats of solvation measure the total strength of the M—O bonds while, as already pointed out, the stretching force constants measure their resistance to a limited deformation. As the potential curves of different M—O bonds generally do not conform, the two quantities cannot be expected to vary according to quite the same pattern between different systems. The minimum at Cd^{2+} nevertheless persists also in the heats of solvation, both for

Table 9. Solvation enthalpies,³⁶ $\Delta H_{\text{sol}}^\circ$ and coordination bond energies,^{9,5} CBE, of Zn^{2+} , Cd^{2+} and Hg^{2+} (kJ mol^{-1}).

	$-\Delta H_{\text{sol}}^\circ$		CBE		
	H_2O	DMSO	Cl^-	Br^-	I^-
Zn^{2+}	2063	2123	2590	2530	2460
Cd^{2+}	1831	1898	2360	2340	2290
Hg^{2+}	1845	1921	2570	2540	2520

DMSO and water,³⁶ Table 9. As expected, it is more marked for the softer ligand DMSO. The total bond strength is considerably higher for Zn^{2+} than for Hg^{2+} in both cases.

For the gaseous halides, the coordinate bond energies,^{9,5} i.e. the enthalpy changes for the reactions $\text{MX}_2(\text{g}) \rightarrow \text{M}^{2+}(\text{g}) + 2\text{X}^-$, provide a measure of the total strength of the $\text{M}-\text{X}$ bonds. For all three ligands, the minimum at Cd^{2+} is again evident, Table 9. For the complexes of the very soft ligand I^- , the total bond strength is even higher for Hg^{2+} than for Zn^{2+} , while for the less soft Br^- they are practically equal. For the least soft halide Cl^- , the bond strength is again higher for Zn^{2+} than for Hg^{2+} . This ligand thus reverts to a pattern similar to that found for DMSO and water. As might be expected, however, the difference between Zn^{2+} and Hg^{2+} is much smaller for Cl^- than for the considerably harder oxygen donors.

Conclusion

The Raman spectra confirm that the acceptors Zn^{2+} , Cd^{2+} and Hg^{2+} form DMSO solvates coordinated via oxygen not only in solids but also in solutions. They clearly indicate an increase of the covalency of the $\text{M}-\text{O}$ interaction in the order $\text{Zn}^{2+} < \text{Cd}^{2+} < \text{Hg}^{2+}$, and also a simultaneous decrease of its electrostatic character. These variations thus counteract each other which results in a minimum of $\text{M}-\text{O}$ bond strength at Cd^{2+} , as is also found from other evidence. The $\text{M}-\text{O}$ bonds are more covalent in the DMSO solvates than in the hydrates, but the bond strength minimum at Cd^{2+} nevertheless persists also for the harder water ligand.

Acknowledgements. We have been fortunate to have the advice of Dr. Georg Johansson, Stockholm, on the X-ray measurements, and of Dr. Ragnar

Larsson, Lund, on the Raman and infrared spectra. We are most grateful for their valuable and generous help.

Our thanks are also due to Professor Kåre Larsson who made the Raman spectrophotometer available. The infrared spectra have been recorded by Dr. Jan Lindgren, Uppsala and Mrs. Karin Trankell, Lund.

We gratefully acknowledge the support given to these investigations by "Naturvetenskapliga forskningsrådet" (The Swedish Natural Science Research Council).

REFERENCES

- Gaizer, F. and Johansson, G. *Acta Chem. Scand.* 22 (1968) 3013.
- a. Sandström, M. *Acta Chem. Scand. A* 32 (1978) 627; b. Sandström, M. *Thesis*, Royal Institute of Technology, Stockholm 1978.
- Wells, A. F. *Structural Inorganic Chemistry*, Clarendon Press, Oxford 1975.
- Waters, D. N. and Kantarci, Z. *J. Raman Spectrosc.* 6 (1977) 251.
- Smith, J. H. and Brill, T. B. *Inorg. Chim. Acta* 18 (1976) 225.
- Sandström, M. and Johansson, G. *Acta Chem. Scand. A* 31 (1977) 132.
- Sandström, M. *Acta Chem. Scand. A* 31 (1977) 141.
- Grdenić, D. *Q. Rev. Chem. Soc.* 19 (1965) 303; *Angew. Chem. Int. Ed. Engl.* 12 (1973) 435.
- Brusset, H. and Madaule-Aubry, F. *Bull. Soc. Chim. Fr.* 10 (1966) 3122 and references therein.
- Biscarini, P., Fusina, L., Nivellini, G. D., Mangia, A. and Pelizzi, G. *J. Chem. Soc. Dalton Trans.* (1973) 159; (1974) 1846.
- Brotherton, P. D. and White, A. H. *J. Chem. Soc. Dalton Trans.* (1973) 2698.
- Sagisawa, K., Kitahama, K., Kiriya, H. and Kiriya, R. *Acta Crystallogr. B* 30 (1974) 1603 and references therein.
- Aurivillius, K. and Stålhandske, C. *Acta Chem. Scand. A* 30 (1976) 735 and references therein.
- Leligny, H., Frey, M. and Monier, J. C. *Acta Crystallogr. B* 28 (1972) 2104 and references therein.
- Brodersen, K., Thiele, G. and Götz, G. *Z. Anorg. Allg. Chem.* 401 (1973) 217.
- Biscarini, P., Fusina, L., Nivellini, G. and Pelizzi, G. *J. Chem. Soc. Dalton Trans.* (1977) 664.
- Sandström, M. and Liem, D. H. *Acta Chem. Scand. A* 32 (1978) 509.
- Grdenić, D., Sikirica, M. and Vicković, I. *Acta Crystallogr. B* 33 (1977) 1630.
- Gerken, V. A. and Pakhomov, V. I. *Zh. Strukt. Khim.* 10 (1969) 753.

20. Brodersen, K. *Acta Crystallogr.* 8 (1955) 723.
21. Weidenhammer, K. and Ziegler, M. L. Z. *Anorg. Allg. Chem.* 434 (1977) 152.
22. White, J. G. *Acta Crystallogr.* 16 (1963) 397.
23. Barr, R. M. and Goldstein, M. J. *Chem. Soc. Dalton Trans.* (1976) 1593.
24. Herlinger, A. W. *Spectrosc. Lett.* 8 (1975) 787.
25. Ferguson, G., Jeffreys, J. A. D. and Sim, G. A. *J. Chem. Soc. B* (1966) 454.
26. Clegg, W., Brown, M. L. and Wilson, L. J. A. *Acta Crystallogr. B* 32 (1976) 2905.
27. Kamenar, B. and Nagl, A. *Acta Crystallogr. B* 32 (1976) 1414.
28. Fenn, R. H. *Acta Crystallogr.* 20 (1966) 24.
29. Pakhomov, B. I., Fedorov, P. M., Alymov, I. M., Ivanova-Korfini, I. N. and Semin, G. K. *Izv. Akad. Nauk. SSSR Ser. Fiz.* 39 (1975) 2519 and references therein.
30. Clegg, W., Greenhalgh, D. A. and Straughan, B. P. J. *Chem. Soc. Dalton Trans.* (1975) 2591.
31. Johansson, G. and Sandström, M. *Acta Chem. Scand. A* 32 (1978) 109.
32. Sandström, M. and Persson, I. *Acta Chem. Scand. A* 32 (1978) 95.
33. Johansson, G. *Acta Chem. Scand.* 25 (1971) 2787, 2799.
34. a. Gallagher, P. K. and King, E. L. *J. Am. Chem. Soc.* 82 (1960) 3510; b. Arnek, R. *Ark. Kemi* 24 (1965) 531.
35. a. Åhlberg, I. and Leden, I. *Transactions of the Royal Institute of Technology*, Stockholm 249 (1972) 17; b. Sjöberg, S. *Acta Chem. Scand. A* 31 (1977) 705.
36. Åhrland, S., Kullberg, L. and Portanova, R. *Acta Chem. Scand. A* 32 (1978) 251.
37. Arnek, R. and Poceva, D. *Acta Chem. Scand. A* 30 (1976) 59.
38. Åhrland, S., Persson, I. and Portanova, R. *To be published*.
39. Criss, C. M. and Salomón, M., In Covington, A. K. and Dickinson, T. Eds., *Physical Chemistry of Organic Solvent Systems*, Plenum, London and New York 1973, Chapter 2, Part 4, Appendix 2.11.15.
40. Åhrland, S. and Björk, N.-O. *Acta Chem. Scand. A* 30 (1976) 249, 257.
41. Leden, I. Z. *Phys. Chem. Abt. A* 188 (1941) 160.
42. Vanderzee, C. E. and Dawson, H. J., Jr. *J. Am. Chem. Soc.* 75 (1953) 5659.
43. Mironov, V. E., Kulba, F. Y. and Nazarov, V. A. *Russ. J. Inorg. Chem.* 8 (1963) 470.
44. Ohtaki, H., Maeda, M. and Ito, S. *Bull. Chem. Soc. Jpn.* 47 (1974) 2217.
45. Pocev, S., Triolo, R. and Johansson, G. *Acta Chem. Scand. A* 32 (1978). *In press*.
46. Åhrland, S. and Björk, N.-O. *Acta Chem. Scand. A* 28 (1974) 823.
47. West, C. D. Z. *Kristallogr. A* 91 (1935) 980.
48. Sandström, M. *Acta Chem. Scand. A* 32 (1978) 519.
49. Montgomery, H. and Lingafelter, E. C. *Acta Crystallogr.* 17 (1964) 1295; 20 (1966) 728.
50. Ferrari, A., Braibanti, A., Manotti Lanfredi, A. M. and Tiripicchio, A. *Acta Crystallogr.* 22 (1967) 240.
51. Ray, S., Zalkin, A. and Templeton, D. H. *Acta Crystallogr. B* 29 (1973) 2741.
52. Black, W. H., Griffith, E. A. H. and Robertson, B. E. *Acta Crystallogr. B* 31 (1975) 615.
53. Bol, W., Gerrits, G. J. A. and van Panthaleon van Eck, C. L. *J. Appl. Crystallogr.* 3 (1970) 486.
54. Sandström, M. *Acta Chem. Scand. A* 32 (1978) 527.
55. Berney, C. W. and Weber, J. H. *Inorg. Chem.* 7 (1968) 283.
56. Karlsson, R. and Karrman, K. J. *Talanta* 18 (1971) 459.
57. Schwarzenbach, G. *Complexometric Titrations*, Methuen, London 1957.
58. Reynolds, W. L. *Prog. Inorg. Chem.* 12 (1970) 1.
59. Martin, D. and Hauthal, H. G. *Dimethyl Sulphoxide*, van Nostrand Reinhold, Wokingham, Berkshire 1975, pp. 448–449.
60. Johansson, G. *Acta Chem. Scand.* 20 (1966) 553.
61. Johansson, G. and Sandström, M. *Chem. Scr.* 4 (1973) 195.
62. Milberg, M. E. *J. Appl. Phys.* 29 (1958) 64.
63. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
64. *International Tables of X-Ray Crystallography*, Vols. 3 and 4, Kynoch Press, Birmingham 1968 and 1974, respectively.
65. Stewart, R. F., Davidson, E. R. and Simpson, W. T. J. *Chem. Phys.* 42 (1965) 3175.
66. Narten, A. H. and Levy, H. A. *J. Chem. Phys.* 55 (1971) 2263.
67. Breit, G. *Phys. Rev.* 27 (1926) 362.
68. Dirac, P. A. M. *Proc. R. Soc. London A* 111 (1926) 405.
69. Dwiggin, C. W. and Park, D. A. *Acta Crystallogr. A* 27 (1971) 264.
70. Levy, H. A., Danford, M. D. and Narten, A. H. *Data Collection and Evaluation with an X-Ray Diffractometer Designed for the Study of Liquid Structure*, Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge 1966.
71. Thomas, R., Shoemaker, C. L. and Eriks, K. *Acta Crystallogr.* 21 (1966) 12.
72. Björk, N. O. and Cassel, A. *Acta Chem. Scand. A* 30 (1976) 235.
73. Berglund, B., Thomas, J. O. and Tellgren, R. *Acta Crystallogr. B* 31 (1975) 1842.
74. Seip, H. M. in *Molecular Structure by Diffraction Methods*, Vol. 1, p. 53, *Specialist Periodical Reports*, The Chemical Society, London 1973.

75. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Elsevier, Amsterdam 1968.
76. Müller, A. and Nagarajan, G. *Z. Naturforsch. Teil B* 21 (1966) 508.
77. Shannon, R. D. and Prewitt, C. T. *Acta Crystallogr. B* 25 (1969) 925.
78. a. Richardson, M. F., Franklin, K. and Thompson, D. M. *J. Am. Chem. Soc.* 97 (1975) 3204; b. Oleksyn, B. J., Stadnicka, K. M. and Hodorowicz, S. A. *Acta Crystallogr. B* 34 (1978) 811.
79. Barrow, M., Bürgi, H. B., Johnson, D. K. and Venanz, L. M. *J. Am. Chem. Soc.* 98 (1976) 2356.
80. Cohn, H. J. *J. Chem. Soc.* (1952) 4282.
81. a. Horrocks, W. D. and Cotton, F. A. *Spectrochim. Acta* 17 (1961) 134; b. Forel, M.-T. and Tranquille, M. *Ibid.* 26 A (1970) 1023.
82. Cotton, F. A., Francis, R. and Horrocks, W. D., Jr. *J. Phys. Chem.* 64 (1960) 1534.
83. Drago, R. S. and Meek, D. *J. Phys. Chem.* 65 (1961) 1446.
84. Selbin, J., Bull, W. E. and Holmes, L. H., Jr. *J. Inorg. Nucl. Chem.* 16 (1961) 219.
85. Currier, W. F. and Weber, J. H. *Inorg. Chem.* 6 (1967) 1539 and references therein.
86. Bennett, M. J., Cotton, F. A., Weaver, D. L., Williams, R. J. and Watson, W. H. *Acta Crystallogr.* 23 (1967) 788.
87. Kawano, Y. and Osorio, V. K. L. *J. Inorg. Nucl. Chem.* 39 (1977) 702.
88. Jones, L. H. *Coord. Chem. Rev.* 1 (1966) 351.
89. a. Hester, R. E. and Plane, R. A. *Inorg. Chem.* 3 (1964) 768, 769; b. Macklin, J. W. and Plane, R. A. *Ibid.* 9 (1970) 821.
90. Bulmer, J. T., Irish, D. E. and Ödberg, L. *Can. J. Chem.* 53 (1975) 3806.
91. Jones, L. *Inorganic Vibrational Spectroscopy*, Marcel Dekker, New York 1971, Vol. 1, pp. 48, 95.
92. Klemperer, W. J. *Chem. Phys.* 25 (1956) 1066 and *J. Electrochem. Soc.* 110 (1963) 1023 and references therein.
93. Vil'kov, L. V., Rambidi, N. G. and Spiridonov, V. P. *J. Struct. Chem.* 8 (1967) 715 and references therein.
94. Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*, van Nostrand, New York 1945, p. 172.
95. Pearson, R. G. and Mawby, R. J. In Gutmann, V., Ed., *Halogen Chemistry*, Academic, London and New York 1967, Vol. 3.

Received March 29, 1978.

Acta Chem. Scand. Ser. A Reg. No.:

Text pages: 17

Received:

Other sheets: 4

Correspondance and proofs should be sent to:

Fil.kand. Ingmar Persson, Oorganisk kemi 1, Kemicentrum,
Lund Universitet, Box 740, S-220 07 Lund 7, Sverige.

Running titles: Persson

Structure of $\text{Zn}(\text{DMSO})_6^{2+}$

The Crystal Structure of Hexakis(dimethylsulfoxide)zinc(II)
Perchlorate and the structure of the Hexakis(dimethylsulfoxide)
zinc(II) Ion in Dimethylsulfoxide Solution.

INGMAR PERSSON

Inorganic Chemistry 1, Chemical Center, University of Lund,
P.O. Box 740, S-220 07 Lund 7, Sweden.

The compound $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ crystallizes in the trigonal space group $\underline{P31c}$ (No.159) with $\underline{a} = 12.006(3)$, $\underline{c} = 12.578(9)$ Å and $\underline{z} = 2$. The X-ray investigation was based on 817 independent reflections collected with an automatic singel-crystal diffractometer of the type CAD-4, using MoK_α radiation. The structure consists of discrete hexakis(dimethylsulfoxide)zinc(II) complex ions and perchlorate ions. The zinc atom coordinates six DMSO molecules through the oxygen atoms, forming an almost regular octahedron. A structural investigation of the hexakis(dimethylsulfoxide)zinc(II) ion has also been performed in dimethylsulfoxide solution, using a large-angle θ - θ diffractometer for X-ray diffraction measurements on liquids. The average Zn-O bond length is 2.110 Å in the solid state and 2.127 Å in dimethylsulfoxide solution, the corresponding Zn-S distances are 3.135 Å and 3.147 Å, respectively.

The configuration of zinc(II) is usually either octahedral or tetrahedral.¹ With most unidentate ligands coordinating via oxygen octahedral complexes are formed. Many structural investigations of crystals containing the hexaaquazinc(II) ion, $\text{Zn}(\text{OH}_2)_6^{2+}$, have been reported.²⁻⁸ The structure of the hexaaquazinc(II) ion has also been determined in concentrated aqueous solutions.⁹⁻¹⁰ The average Zn-O bond length in this ion is 2.09 Å in both crystals and solutions. Also organic ligands coordinating via oxygen, such as pyridine-N-oxide, form regular octahedral structures¹¹ with an average Zn-O bond length of 2.102 Å.

The solvation of the divalent d^{10} ions, zinc(II), cadmium(II) and mercury(II) in dimethylsulfoxide solution has previously been studied by means of calorimetry, large angle X-ray diffraction on solutions and Raman and infrared spectroscopy.¹²⁻¹³ For cadmium(II) and mercury(II) the structures have been determined in both solid state and solution.¹³⁻¹⁵ For zinc(II), spectroscopic measurements show that the dimethylsulfoxide is coordinated via the oxygen atom.¹³ The preparation of the compound $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ has been described previously.¹⁶ This compound also crystallizes from saturated DMSO solutions of zinc(II) perchlorate. Judging from the empiric formula, the zinc(II) ion probably coordinates six DMSO molecules in an octahedral configuration. The coordination geometry of the DMSO solvated zinc(II) ion in solution plays a fundamental part in the discussion of the thermodynamics of the complex formation of zinc(II) in DMSO solution.¹⁷

In an earlier paper,¹³ it was reported that the solubility of $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ in DMSO is only 0.29 M. This concentration is too low to allow a study of the solvate structure by means of X-ray diffraction measurements. It is, however, possible to prepare a supersaturated 0.70 M solution. With this solution the structure of the zinc(II) DMSO solvate can be determined.



EXPERIMENTAL

Preparation of crystals. The crystals were prepared and analyzed as described previously.¹⁶ They are slightly hygroscopic; single-crystals decompose in air to powder in two days. The crystals also react with organic compounds such as stopcock and silicon grease and different types of glue. Among these, epoxy glues work satisfactorily, however. The density of the crystals was determined by the displacement method with benzene.

X-ray data collection. Weissenberg photographs revealed the Laue class $\bar{3}m$ and the systematic absences: $hh2\bar{h}l$; $l=2n+1$ and $hkil$; $l=2n$, indicating the space groups $P\bar{3}1c$ or $P31c$.

The intensity data were collected by an automatic single-crystal diffractometer of type CAD-4, at 246 ± 1 K, in order to avoid extensive decomposition of the crystal. Zr-filtrated MoK_α -radiation ($\lambda = 0.71300$ Å) was used. A hexagonal prismatic crystal with all edges ≈ 0.20 - 0.25 mm was used. The unit cell dimensions were obtained from the θ values of 25 reflections. Crystal data: $a = 12.006(3)$, $c = 12.578(9)$ Å, $V = 1570.2(2)$ Å³, $Z = 2$, $D_m = 1.54(2)$, $D_x = 1.55$ g cm⁻³, $\mu(\text{MoK}_\alpha) = 14.1$ cm⁻¹.

The ω - 2θ scan technique was employed, with a scan interval $\Delta\omega = 1.00 + 0.15 \tan \theta$. The background measurements were performed by increasing $\Delta\omega$ with $1/4$ on both sides. 2141 independent reflections in the range $3^\circ \leq \theta \leq 32^\circ$ were measured. Among these, 7 strong reflections were deleted because they were too intense for the counter. Another 810, with $I < 3\sigma_c(I)_s$ were deleted as being too weak. The values of $\sigma_c(I)$ were based on counting statistics. Three reflections were selected as standard. The fluctuations in the intensities of the standard reflections were irregular and less than 8%. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects.

X-ray data collection from solutions. The X-ray scattering of MoK_α -radiation ($\lambda=0.71069 \text{ \AA}$) from the free surface of the DMSO solution was measured as described in previous papers.¹⁸⁻¹⁹ The solution was enclosed in an air-tight shield, with cylindrical beryllium windows for the X-rays. The scattered intensity was measured at discrete points between the θ values 1.0° and 62.5° , where 2θ is the scattering angle. Intervals of 0.1° for $1.0^\circ \leq \theta \leq 30.0^\circ$ and 0.25° for $20.0^\circ \leq \theta \leq 62.5^\circ$ were used. 40 000 counts were accumulated twice for each point, corresponding to a statistical error of 0.35%. All measurements were performed at $25 \pm 1^\circ\text{C}$.

Preparation of the solution. The DMSO solution investigated was prepared by dissolving $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ in DMSO at around 90°C . The solution was cooled to room temperature very slowly. The 0.70 M solution obtained was metastable and had to be handled with care. On shaking solid $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$ immediately precipitated.

Computer programs. The computer programs used for determining the crystal structure are the same as listed elsewhere.²⁰ All calculations of the structures in solution were made by the KURVLR and PUTSLR computer programs²¹. All calculations were carried out on a UNIVAC 1100/80 computer at the computer Center, University of Lund.

STRUCTURE DETERMINATION OF THE SOLID SOLVATE

In the space group $\underline{P31c}$ (no.159), the zinc ions were placed in $\underline{z} = 0.25$ (2(b)), which fixed the origin. The chlorine atoms were given $\underline{z}$ coordinates close to 0.00 and 0.75 in the special positions 2(a) and 2(b), respectively. This was in accordance with the Patterson map. From a difference Fourier map, the positions of the sulfur, oxygen and carbon atoms in the DMSO molecules could be identified. With these atoms isotropic, full-matrix least-squares refinements, minimizing $\sum w(|F_o| - |F_c|)^2$, gave $R=0.14$ ($R_w=0.18$).

The conventional R -value is defined as $R = \sum(|F_o| - |F_c|) / \sum |F_o|$, and the weighted as $R_w = ((\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$. A refinement in the space group $P\bar{3}1c$ was unsuccessful.

At this stage a difference Fourier map revealed the positions of three oxygen atoms in each perchlorate ion. The remaining oxygen, on the three-fold axis, is impossible to locate, evidently due to a very high temperature coefficient. In the following calculations, a high, fixed value was therefore given to this coefficient. Reflections with $\theta > 23^\circ$ are all very weak and were therefore excluded in the final refinements. This resulted in $R = 0.073$ and $R_w = 0.089$ for the remaining 817 independent reflections. A total of 92 parameters, including two scale factors, were varied in the final refinements. In the last cycle the shifts in the parameters were less than 1% of the e.s.d.'s. The weighting scheme was $w = 1/\sigma_c^2 + 0.040|F_o|^2 + 3.00$ which, according to a weight analysis, gave a satisfactory error distribution. The largest remaining peak found in the final difference Fourier map was $1.35 \text{ e}\text{\AA}^{-3}$. This peak was close to the position of the sulfur atom, the distance being 0.85 Å. Definite H atom positions could not be ascertained. The scattering factors used in the calculations were taken from International Tables for X-Ray Crystallography, Vol. IV. The final refined parameter values are given in Tables 1 and 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure consists of hexakis(dimethylsulfoxide)zinc(II) cations, $\text{Zn}(\text{DMSO})_6^{2+}$, with a three-fold axis, and of perchlorate ions, ClO_4^- . A stereoscopic view of the molecular geometry of the DMSO solvated zinc(II) ion is given in Fig.1, and a stereoscopic view of the unit cell in Fig.2. Some intramolecular distances and angles are listed in Table 3.

The $\text{Zn}(\text{DMSO})_6^{2+}$ complex. Each zinc(II) ion coordinates six DMSO molecules through the oxygen atoms. The resulting coordination polyhedron around the zinc(II) ion is a slightly distorted

octahedron with an average Zn-O bond length of 2.110 Å, Table 3. The sulfur atoms also form a somewhat irregular octahedron around zinc, with an average Zn-S distance of 3.135 Å. The slight distortion of the octahedron around zinc is shown by a torsion angle of 57.3 degrees along the three-fold axis and a distance of 0.017 Å between the zinc atom and the centre of gravity of the oxygen octahedron.

The average S-O and S-C distances with the pyramidal DMSO molecule are 1.494 and 1.790 Å, respectively, which agree well with distances found for other solvates where DMSO is coordinated via oxygen.²² The S-O bond is somewhat longer and consequently slightly weaker than in free DMSO.²³ This is also indicated by the raman and infrared spectra¹³ which show a lowering of the S-O stretch frequency on the coordination of DMSO via oxygen. The S-C bond is, on the other hand, shorter, and consequently stronger, in the coordinated DMSO. Consistent with this, the S-C stretching frequency is higher in coordinated than in free DMSO.¹³

The average Zn-O-S angle is 120° , Table 3, a value found for the M-O-S angle in many DMSO solvates. It is obvious, that the hybridization around the oxygen atom in DMSO determines this angle. The angles within the coordinated DMSO molecules are much the same as in other DMSO complexes^{14,15,24,25} and in free DMSO.²³

The ClO_4^- ion. The four oxygen positions 011, 012, 021 and 022 belong to the two perchlorate ions. Two of these, 011 and 021, are situated around a three-fold axis and fairly well-defined. The bond lengths Cl-O for these oxygens are 1.43 and 1.48 Å (Table 3), i.e. close to the bond lengths generally found in perchlorates, 1.42-1.43 Å.²⁶ The other two oxygen positions 012 and 022 are on the three-fold axis. Distorted perchlorate ions are also found e.g. in the structures of $\text{Ag}(\text{DMSO})_2(\text{ClO}_4)_2$,²⁴ $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$,¹⁴ $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$,¹⁵ $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$.²⁵ A survey of such structures is given in Ref 24.

STRUCTURE DETERMINATION IN SOLUTION

Data reduction and correction. The measured intensities were corrected for the background and normalized to a stoichiometric unit of volume, V , corresponding to the average volume per zinc(II) ion in the solution. The normalization was done by comparing the high angle region of the corrected intensities with the sum of the independent coherent scattering and the fraction of the incoherent scattering reaching the counter. No corrections for the absorption were applied.

RHF scattering factors, f , were used²⁷ for the neutral atoms and zinc(II). For hydrogen, the spherical form factors proposed by Stewart et.al. were employed.²⁸ No absorption corrections were necessary. Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were applied to all atoms.²⁷ The incoherent scattering factors, I_{incoh} , were taken from the same sources as before.²⁹ Corrections for the Breit-Dirac factor in the form appropriate for a radiation counter, $(\lambda/\lambda')^3$, where $\lambda' = \lambda + \Delta\lambda$ and $\Delta\lambda = \frac{h}{m \cdot c}(1 - \cos 2\theta)$, were applied.²⁷ The reduced intensity curves, $i(s)$, and the electronic radial distribution functions, $D(r)$, with $M = \text{Zn}$, were calculated as described previously.¹³ Small spurious peaks below 1.5 Å in the $(D(r)_{\text{obs}} - D(d)_{\text{calc}})$ function which could not be related to interatomic distances, were removed by a Fourier transformation procedure.³ The calculation of intramolecular intensity contributions to the reduced intensity curve and the electronic radial distribution function were carried out as described previously.^{21,30}

RESULTS

Intensity curve and radial distribution (RDF). The electronic radial distribution function (RDF), $D(r) - 4\pi r^2 \rho_0$, is given in Fig. 3. The peak found at about 3.2 Å in the radial distribution function (RDF) fits with the zinc-sulfur distance, found in the solid state of $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$, Table 3. The expected zinc-oxygen distance at about 2.1 Å could not be seen in the RDF, however.

The intramolecular DMSO distances should occur at about 1.48 (S-O),

1.81(S-C), 2.66(O-C) and 2.77 Å(C-C). The peak at 1.6-1.7 Å, Fig. 4 is due to the S-O and S-C distances. Expected Cl-O and O-O distances within the tetrahedral ClO_4^- ion are 1.43 and 2.33 Å, respectively.²⁶ The broad peaks at 5-6 and 9-10 Å are very probably caused by interactions between DMSO molecules.

The sum of all calculated intramolecular reduced intensity contributions, $i_{\text{calc}}(\underline{s})$, are compared with experimental $i_{\text{obs}}(\underline{s})$ curves in Fig. 4, after multiplication by $\underline{s}$.

Least-squares refinements. This procedure was carried out as described previously.¹³ The model finally selected consisted of the following parts.

1. In the $\text{Zn}(\text{DMSO})_6^{2+}$ complex, the distances Zn-O and Zn-S, $\underline{d}$, the coefficients $\underline{b}$ of their temperature factors $\exp(-\underline{b}\underline{s}^2)$, and the number of distances, $\underline{n}$, were refined. Also the contribution from the O-O interactions, was introduced, assuming an octahedral arrangement around the zinc atom.
2. Intramolecular DMSO bond distances and temperature factor coefficients were taken from a study of pure DMSO.³¹ These distances agree very well with the values found in solid and gaseous state.^{23,32} In this way, all DMSO molecules, bonded as well as non-bonded, were accounted for.
3. The parameters of the perchlorate ion were the same as used previously.¹³

The parameter values from the refinements in the range $5.50 \leq \underline{s} \leq 15.25 \text{ \AA}^{-1}$ are summarized in Table 4. The standard deviations given in Table 4 are those calculated in the least-squares procedure.

DISCUSSION

The zinc(II) ion coordinates six DMSO molecules through the oxygen atoms in an octahedral configuration. A zinc(II) solvate of the same type is formed with pyridine-N-oxide.¹¹ In the solid solvates, the Zn-O distances are 2.110 and 2.102 Å, respectively. The Zn-O distance of 2.127 Å found in the zinc(II) solvate in DMSO solution is very close to the values found in the solid.

Zinc(II) is a hard acceptor preferring hard donor atoms like oxygen. The bonds formed are of a mainly electrostatic character. Among the important oxygen ligands coordinated is water. The structures of a large number of crystalline zinc(II) hydrates have been reported.²⁻⁸ In all of these, six water molecules are octahedrally coordinated. The average Zn-O distance ranges from 2.078 to 2.107 Å, with an overall average of 2.092 Å. This value is very close to the distances found in the hexahydrated zinc(II) ion in aqueous solution, 2.08 and 2.092 Å.^{9,10}

A comparison between the Zn-O distances in the hexahydrate and the DMSO and pyridine-N-oxide hexasolvates shows that the distance is significantly shorter in the hydrate. Water is thus more strongly bonded than organic solvents coordinating via oxygen. The oxygen in organic solvents as DMSO and pyridine-N-oxide acts as a less hard donor than the water oxygen.

From the average bond lengths of the zinc(II) hydrates and solvates, the ionic radius of the zinc(II) ion in octahedral configuration can be derived. The radii of oxygen are taken as 1.35 Å in the organic ligands where oxygen is two-coordinated and as 1.36 Å in the hydrates where oxygen is three-coordinated.³³ From the solid DMSO and pyridine-N-oxide hexasolvates a value of, $r(\text{Zn}^{2+}) = 0.76$ Å is calculated and from the DMSO hexasolvate in solution, $r(\text{Zn}^{2+}) = 0.78$ Å. From the hydrates in solid phase and solution $r(\text{Zn}^{2+}) = 0.73$ Å is found. The value calculated from oxide and fluoride structures by Shannon and Prewitt,³³ 0.745 Å, is very close to the value derived from the present measurements.

The enthalpy change of the transfer¹² $\text{Zn}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{DMSO})$, $\Delta H_{\text{tr}}^{\circ} = -60 \text{ kJ mol}^{-1}$, indicates that the solvation of the zinc(II) ion is favoured in DMSO relative to water, in spite of the fact that the Zn-O bonds are shorter and consequently stronger in water than in DMSO. An obvious explanation of this apparent contradiction is that more energy has to be spent in water to break the solvent structure. This difference must evidently be $>60 \text{ kJ}$, the value of $\Delta H_{\text{tr}}^{\circ}$. It should be noted that for mercury(II), the bond distances Hg-O are about the same,¹³ $2.40 \text{ \AA}$, in aqueous and DMSO solution, while the value of $\Delta H_{\text{tr}}^{\circ} = -76 \text{ kJ mol}^{-1}$.

ACKNOWLEDGEMENTS

My thanks are due to Dr Åke Oskarsson for his continuous readiness to help during the crystallographic part of this work. I am also most indebted to Professor Oliver Lindqvist and Mr Åke Iverfeldt who recorded the data of the zinc(II) perchlorate in DMSO solution on the X-ray diffractometer for liquids of the Department of Inorganic Chemistry, University of Göteborg. Professor Sten Åhrland is gratefully thanked for his stimulating and continuous interest in this investigation.

REFERENCES

1. Wells, A.F. Structural Inorganic Chemistry, 4th Ed., Oxford 1975.
2. Yü, S.H. and Bevers, C.A. Z. Krist. 82 (1932) 297.
3. Montgomery, H. and Lingafelter, E.C. Acta Crystallogr. 17 (1964) 1295.
4. Ferrari, A., Braibanti, A., Manotti Lanfredi, A.M. and Tiripicchio, A. Acta Crystallogr. 22 (1967) 240.
5. Ray, S., Zalkin, A. and Templeton, D.H. Acta Crystallogr. B29 (1973) 2741.
6. Black, W.H., Griffith, E.A.H. and Robertson, B.E. Acta Crystallogr. B31 (1975) 615.
7. Whitnall, J., Kennard, C.H.L., Nimmo, J. and Moore, F.H. Cryst. Struct. Comm. 4 (1975) 717.
8. Gupta, M.P. and Agrawal, J.L. Cryst. Struct. Comm. 6 (1977) 103.
9. Bol, W., Gerrits, G.J.A. and van Panthaleon van Ek, C.L. J. Appl. Cryst. 3 (1970) 486.
10. Ohtaki, H., Yamaguchi, T. and Maeda, M. Bull. Chem. Soc. Japan 49 (1976) 701.
11. O'Connor, C.J., Sim, E. and Carlin, R.L. Inorg. Chem. 16 (1977) 3314.
12. Åhrland, S., Kullberg, L. and Portanova, R. Acta Chem. Scand. A32 (1978) 251.
13. Sandström, M., Persson, I. and Åhrland, S. Acta Chem. Scand. A32 (1978) 607.
14. Sandström, M. Acta Chem. Scand. A32 (1978) 519.
15. Sandström, M. and Persson, I. Acta Chem. Scand. A32 (1978) 95.
16. Åhrland, S. and Björk, N.O. Acta Chem. Scand. A28 (1974) 823.

17. Ahrlund, S., Björk, N.O. and Portanova, R. Acta Chem. Scand. A30 (1976) 270.
18. Johansson, G. Acta Chem. Scand. 20 (1966) 553.
19. Johansson, G. Acta Chem. Scand. 25 (1971) 2787, 2799.
20. Svensson, C. Diss., Institute of Technology, Lund, 1978
21. Johansson, G. and Sandström, M. Chem. Scr. 4 (1973) 195.
22. Persson, I. Diss. University of Lund, Lund, 1980.
23. Viswamitra, M.A. and Kannan, K.K. Nature 209 (1966) 1016.
24. Björk, N.O. and Cassel, A. Acta Chem. Scand. A30 (1976) 235.
25. Sandström, M. Acta Chem. Scand. A32 (1978) 527.
26. Berglund, B., Thomas, J.O. and Tellgren, R. Acta Crystallogr. B31 (1975) 1842.
27. International Tables of X-Ray Crystallography Vol 3 and 4, Kynoch Press, Birmingham 1968 and 1974
28. Stewart, R.F., Davidson, E.R. and Simpson, W.T. J. Chem. Phys. 42 (1965) 3175.
29. Sandström, M. and Johansson, G. Acta Chem. Scand. A31 (1977) 132.
30. Levy, H.A., Danford, M.D. and Narten, A.H. Data Collection and Evaluation with an X-Ray Diffractometer Designed for Study of Liquid Structure, Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge 1966.
31. Ahrlund, S., Hansson, E., Iverfeldt, Å. and Persson, I. To be published.
32. Bastiansen, O. and Viervoll, H. Acta Chem. Scand. 2 (1948) 702.
33. Shannon, R.D. and Prewitt, C.T. Acta Crystallogr. B25 (1969) 925.

Table 1. Final fractional atomic positional parameters with estimated standard deviations in parentheses. The G values are the occupancy factors.

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>G</u>
Zn	1/3	2/3	1/4	0.333
O1	0.1699(12)	0.6293(12)	0.1584(10)	1.000
S1	0.1518(4)	0.7406(4)	0.1313(4)	1.000
C1	0.0728(25)	0.6995(22)	0.0043(16)	1.000
C2	0.0204(19)	0.7261(22)	0.2137(15)	1.000
O2	0.2198(12)	0.5045(13)	0.3443(10)	1.000
S2	0.0890(5)	0.4722(5)	0.3815(4)	1.000
C3	0.0806(23)	0.4209(24)	0.5164(17)	1.000
C4	0.9815(19)	0.3237(24)	0.3240(19)	1.000
C11	0	0	0.0019(14)	0.333
C12	2/3	1/3	0.2639(10)	0.333
O11	0.1145(26)	0.0121(23)	0.0481(15)	1.000
O12	0	0	0.897(7)	0.333
O21	0.6653(25)	0.2166(27)	0.2217(19)	1.000
O22	2/3	1/3	0.369(7)	0.333

Table 2. Final anisotropic thermal parameters ($\text{\AA}^2$) with estimated standard deviations in parentheses. The temperature factor expression used is $\exp[-B_{11}h^2 - \dots - 2B_{12}hk - \dots]$. The isotropic temperature coefficients are given in $\text{\AA}^2$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	0.0051(1)	0.0051(2)	0.005(2)	0.0026(1)	0	0
O1	0.0097(13)	0.0097(13)	0.0081(10)	0.0055(11)	-0.0012(9)	0.0000(9)
S1	0.0073(4)	0.0079(5)	0.0069(3)	0.0039(4)	-0.0002(3)	0.0037(6)
C1	0.0183(32)	0.0162(26)	0.0074(16)	0.0115(25)	-0.0039(18)	0.0010(17)
C2	0.0111(22)	0.0139(26)	0.0084(15)	0.0085(20)	0.0024(14)	-0.0011(16)
O2	0.0114(15)	0.0104(14)	0.0068(9)	0.0067(13)	0.0000(9)	0.0007(9)
S2	0.0100(6)	0.0120(6)	0.0087(4)	0.0058(5)	0.0031(4)	0.0038(4)
C3	0.0165(30)	0.0189(33)	0.0064(13)	0.0125(28)	0.0054(16)	0.0047(17)
C4	0.0079(20)	0.0166(31)	0.0114(20)	0.0046(21)	-0.0013(16)	-0.0016(19)
C11	0.0097(5)	0.0097(5)	0.0185(10)	0.0048(2)	0	0
C12	0.0082(4)	0.0082(4)	0.0118(8)	0.0041(2)	0	0
O11	11.4(6)					
O12	25.0					
O21	12.6(8)					
O22	25.0					

Table 3. Some intramolecular atomic distances (Å) and angles (degrees) in $\text{Zn}(\text{DMSO})_6(\text{ClO}_4)_2(\text{s})$. Estimated standard deviations are given in parentheses.

Zn-O1	2.121(13)	O1-Zn-O1	93.3(5)
Zn-O2	2.098(13)	O2-Zn-O2	91.2(5)
		O1-Zn-O2	85.2(5)
Zn-S1	3.115(4)	O1-Zn-O2	90.4(5)
Zn-S2	3.154(5)	O1-Zn-O2	176.1(5)
S1-O1	1.496(3)	Zn-O1-S1	117.8(7)
S1-C1	1.796(22)	Zn-O2-S2	122.0(8)
S1-C2	1.820(20)		
S2-O2	1.492(13)	O1-S1-C1	104.5(9)
S2-C3	1.790(23)	O1-S1-C2	106.9(9)
S2-C4	1.750(24)	C1-S1-C2	99.6(10)
Cl1-O11	1.43(3)	O2-S2-C3	104.9(10)
Cl1-O12	1.31(9)	O2-S2-C4	106.3(9)
Cl2-O21	1.48(3)	C3-S2-C4	98.9(12)
Cl2-O22	1.32(9)		
		O11-Cl1-O11	104.7(12)
		O11-Cl1-O12	113.9(10)
		O12-Cl2-O12	109.4(11)
		O12-Cl2-O22	109.5(11)

Table 4. Least-squares refinement of the 0.70 M zinc(II) perchlorate DMSO solution. The refined parameters $\underline{d}$ = distance (Å), $\underline{b}$ = temperature factor coefficient (Å²) and $\underline{n}$ = number of distances per metal atom are obtained in the range $5.50 \leq \underline{s} \leq 15.25$ of the reduced intensity curve. Estimated standard deviations are given within parentheses for refined parameters.

Complex	Interaction	Parameter	
$\text{Zn}(\text{DMSO})_6^{2+}$	Zn-O	$\underline{d}$	2.127(5)
		$\underline{b}$	0.0148(9)
	Zn-S	$\underline{d}$	3.147(3)
		$\underline{b}$	0.0158(6)
	Zn-O and Zn-S	$\underline{n}$	6.0(1)
ClO_4^-	Cl-O	$\underline{d}$	1.425
		$\underline{b}$	0.0010
		$\underline{n}$	4
DMSO	S-O	$\underline{d}$	1.496
	S-C	$\underline{d}$	1.805
	S-O and S-C	$\underline{b}$	0.0017

FIGURES

- Fig 1. A stereoscopic view of the $\text{Zn}(\text{DMSO})_6^{2+}$ cation. All atoms are represented by 50% probability ellipsoids.
- Fig 2. A stereoscopic view of the trigonal unit cell.
- Fig 3. The function $D(\underline{r}) - 4\pi \underline{r}^2 \rho_0$ (solid line) compared with sums of calculated peak shapes of the refined model (dashed line). The parameter values used are given in Table 4 and in the text. The difference is shown by the dashed-dotted lines.
- Fig 4. Reduced intensities, $\underline{i}(\underline{s})$, multiplied with $\underline{s}$, for 0.7 M $\text{Zn}(\text{DMSO})_6^{2+}$ solution (left). Experimental values are denoted by dots (the six first are obtained by extrapolation) and values calculated for the refined model by solid lines. The difference between experimental and calculated values, $\underline{s}i_{\text{obs}}(\underline{s}) - \underline{s}i_{\text{calc}}(\underline{s})$, is also shown (right).

Fig. 1.

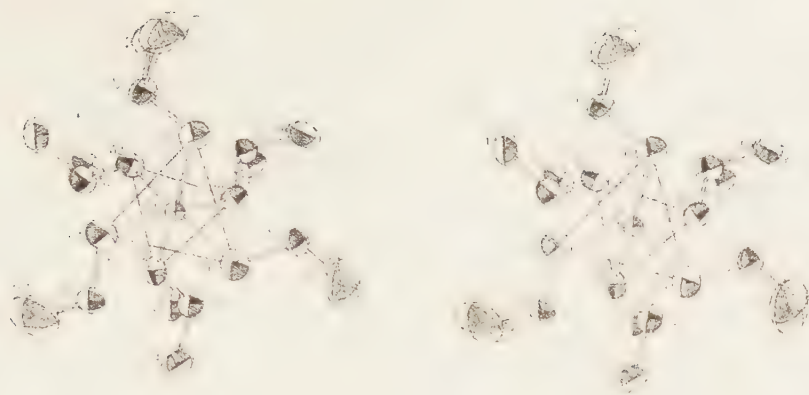


Fig. 2.

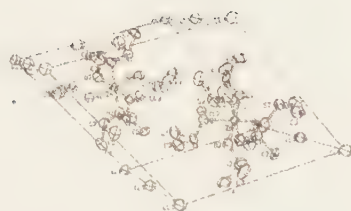
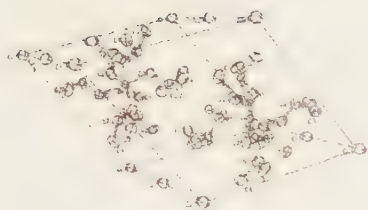


Fig. 3.

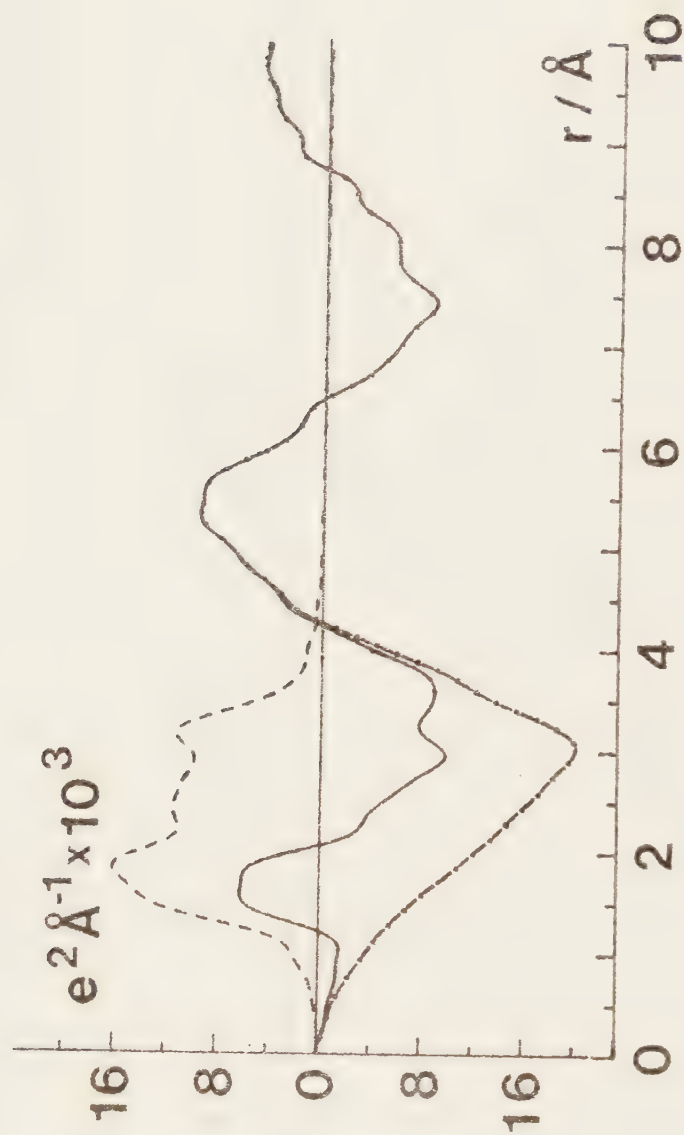
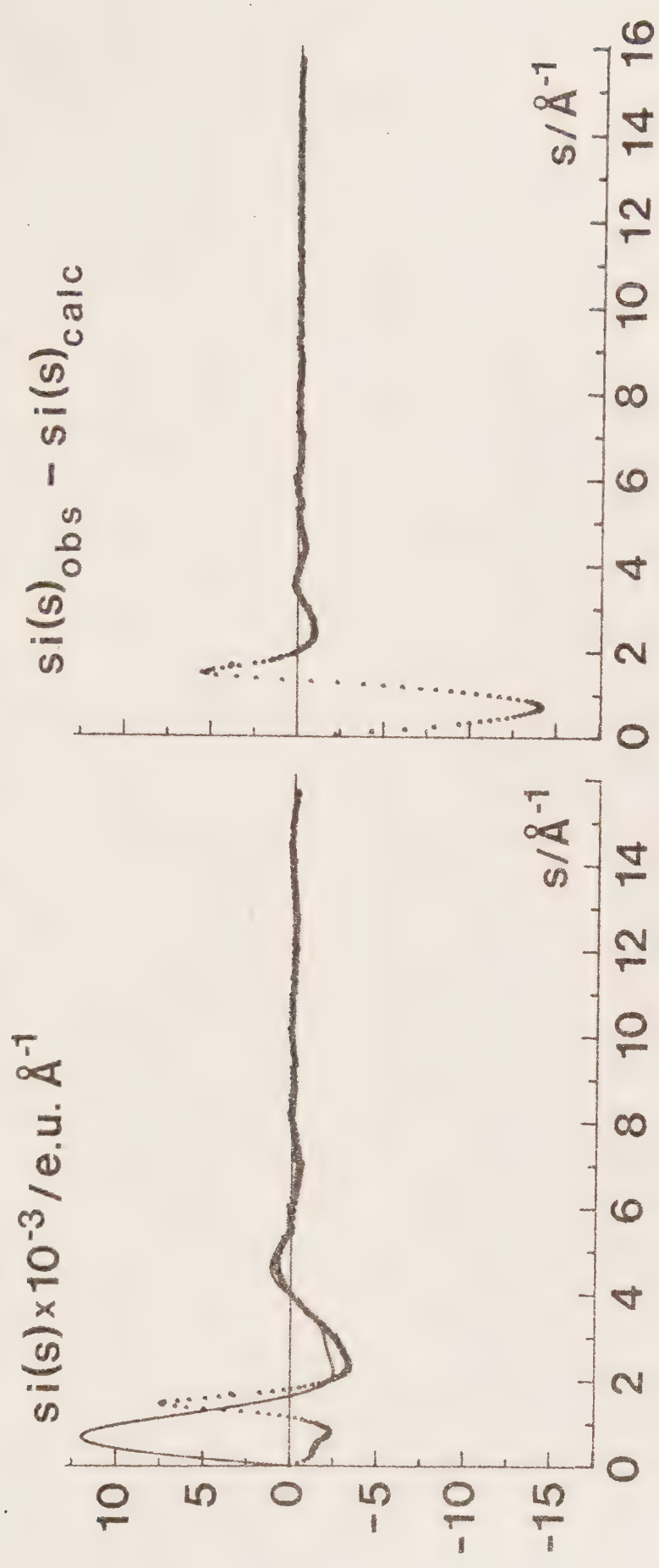


Fig. 4.



Crystal and Molecular Structure of Hexakis(dimethylsulfoxide)-mercury(II) Perchlorate, $[\text{Hg}((\text{CH}_3)_2\text{SO})_6](\text{ClO}_4)_2$

MAGNUS SANDSTRÖM^a and INGMAR PERSSON^b

^a Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden and

^b Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The compound $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 7.418(2)$, $b = 10.831(6)$, $c = 11.241(4)$ Å, $\alpha = 118.37(4)^\circ$, $\beta = 93.10(3)^\circ$, $\gamma = 92.60(3)^\circ$ and $Z = 1$. The X-ray investigation was based on 2001 independent reflections collected with a computer-controlled Syntex $P2_1$ four-circle diffractometer using $\text{MoK}\alpha$ radiation. The structural parameters were refined by least-squares methods to a conventional R value of 0.035.

The structure is built up from discrete hexakis(dimethylsulfoxide)mercury(II) complex ions and perchlorate ions. The mercury atom is coordinated to six DMSO molecules through the oxygen atoms in an almost regular octahedron. The average $\text{Hg}-\text{O}$ bond length is 2.34 Å. The perchlorate group is disordered and performs large librational movements in the absence of hydrogen bonds.

The most common configuration of hexa-coordinated mercury is that of a distorted octahedron, with two short linear bonds.¹ Discrete complexes with regular octahedral coordination seem to be rare, but an example has been found in the compound $[\text{Hg}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ with an $\text{Hg}-\text{O}$ bond length of 2.35(2) Å.² Moreover, X-ray diffraction^{3,4} and Raman⁴ measurements on DMSO and aqueous solutions are consistent with a regular coordination of six solvent molecules to the Hg^{2+} ion. The average $\text{Hg}-\text{O}$ bond lengths are 2.393(5) and 2.41(1) Å,⁴ respectively. For a comparison with the structures found for the solvated ions in solution the crystal structures of the solvates $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$,⁵ $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$,⁶ and $[\text{Hg}((\text{CH}_3)_2\text{SO})_6](\text{ClO}_4)_2$ in the present paper, were determined.

EXPERIMENTAL

Preparation of crystals. Saturated DMSO solutions, 0.94 M at 25 °C, were prepared by dissolving the compound $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ in pure DMSO.⁴ By slow evaporation or by cooling, colourless prismatic crystals of the composition $\text{Hg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$ were formed. The crystals were filtered off and washed with cold acetone. Methods and results of analyses of the crystals are given elsewhere.⁴

The crystals were very hygroscopic and decomposed rapidly in air. Even when stored in a closed tube they decomposed slowly losing DMSO. After two months the average number of DMSO molecules per mercury atom was found to be 5.4(1).

X-Ray data collection. The intensity data were collected at 25 ± 2 °C by a computer-controlled four-circle diffractometer of type Syntex $P2_1$, equipped with a scintillation counter. Graphite-monochromatized $\text{MoK}\alpha$ -radiation ($\lambda = 0.71069$ Å) was used.

A prismatic crystal with maximum dimensions of about 0.1 mm, contained in a capillary, was aligned optically. Approximate positions of 20 reflections were obtained from an oscillation photograph on the diffractometer. These reflections were automatically centred and used in an auto-indexing routine to determine the lattice constants, which were refined using least-squares methods. The unit cell was found to be triclinic with the crystal data: $a = 7.418(2)$, $b = 10.831(6)$, $c = 11.241(4)$ Å, $\alpha = 118.37(4)^\circ$, $\beta = 93.10(3)^\circ$, $\gamma = 92.60(3)^\circ$, $V = 790.9(6)$ Å³, $D_m = 1.76(3)$ and $D_x = 1.82$ g cm⁻³ for $Z = 1$.

The $\theta-2\theta$ scan mode was used for the intensity data collection with different scan speeds, the minimum scan speed being 2° min⁻¹. Stationary background measurements were made on each side of a peak. The total background counting time was equal to the scan time.

The intensity, I , of each reflection was calculated by subtracting the total background count, BG , from the total scan count, SC . The standard deviation, $\sigma(I)$, was obtained from $\sigma(I) = (SC + BG)^{1/2}$. The values obtained were then multiplied with the scan rate to compensate for the different scan speeds. All intensities were corrected for Lorentz and polarization effects and converted to scaled $|F_o|$ values by means of a data reduction program. Of the 2064 possible independent reflections for $2\theta < 45^\circ$, 2001 had intensities larger than $1.96 \sigma(I)$ and were considered observed.

After every 50th reflection three check reflections were measured. Their intensities varied within $\pm 15\%$ during the data collection. They first increased and then slowly decreased, probably due to extinction changes during a gradual decomposition of the crystal. No correction for this was applied.

The absorption coefficient $\mu(\text{MoK}\alpha)$ is 55.7 cm^{-1} . A semi-empirical absorption correction method was used.⁷ The intensities of selected reflections, which had χ values close to 90° and 2θ values evenly distributed over the 2θ range used, were measured for a full flat-cone rotation around the diffraction vector in steps of 10° . The relative intensity variations obtained were used to correct the intensities of all measured reflections in appropriate 2θ -intervals. The largest measured relative reduction in intensity was from 1.00 to 0.63.

Computer programs. The program system supplied by Syntex (XTL version 2)⁸ for a NOVA 24K computer with a disk memory unit, was used for the calculations. In addition, the thermal-ellipsoid plot program for crystal structure illustrations, ORTEP 2, was used.⁹

STRUCTURE DETERMINATION AND REFINEMENTS

Determination of the structure. From a three-dimensional Patterson peak listing one Hg—Cl, three Hg—S and three Hg—O vectors, all with a multiplicity of two, could be identified. The space-group was therefore assumed to be the centrosymmetrical $P\bar{1}$ (No. 2), and the corresponding atomic parameters, with Hg at the origin of the unit cell, were refined by least-squares methods. The positions of the C atoms were found from a subsequent Fourier difference synthesis. Full-matrix least-squares refinements gave $R = 0.070$ ($R_w = 0.096$) with Hg anisotropic.

The conventional R -value is defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, and the weighted as $R_w = (\sum w |F_o - F_c|) / \sum w |F_o|$.

A three-dimensional Fourier difference map was calculated and showed regions of increased electron density at about $1.4 \text{ \AA}$ from the chlorine atoms. Seven more or less distinct peaks with heights between 1.1 and $2.4 \text{ e \AA}^{-3}$ were found. Their locations and relative sizes corresponded approximately to two alternative positions of the ClO_4 group, obtained by rotating it $\sim 60^\circ$ around an axis through the Cl and the highest of the oxygen peaks. This oxygen, O4, was then given a fixed occupancy number 1.0 and the remaining six positions 0.5. After new refinements another Fourier difference synthesis revealed peaks around the C atoms with heights of 0.4 to $0.8 \text{ e \AA}^{-3}$, which could be ascribed to the 18 H atom positions.

Full-matrix least-squares refinements with all non-H atoms anisotropic and with a fixed B -value of $5 \text{ \AA}^2$ for the H atoms gave $R = 0.036$ ($R_w = 0.048$). Finally, also the occupancy numbers of the perchlorate oxygens were allowed to vary, which gave $R = 0.035$ ($R_w = 0.047$).

Test of the absorption correction. Similar final refinements were also performed for data without the semi-empirical absorption correction described above, and gave $R = 0.036$ ($R_w = 0.047$).

The main effect of this absorption correction was to decrease the largest remaining peaks in the final difference Fourier synthesis, which were located around Hg, from 1.4 to $0.9 \text{ e \AA}^{-3}$. The refined parameters were not significantly affected except for the oxygen atoms coordinated to Hg, where the average Hg—O bond distance increased by $0.01 \text{ \AA}$. The data set with the absorption correction was considered to be the better one and was used for all other calculations reported here.

This semi-empirical absorption correction has, in some cases, been found to give almost identical results as those obtained using a Gaussian integration method, for some highly absorbing compounds.¹⁰

Test of non-centrosymmetry. In order to check if deviations from centrosymmetry would occur for the neighbouring atoms of the perchlorate groups, and if the perchlorate positions could be described in a better way, calculations were also performed in the non-centrosymmetric space-group $P1$ (No. 1). However, the R_w values obtained were not, according to statistical tests,¹¹ significantly lower than the corresponding values for $P\bar{1}$. Moreover, some of the anisotropic temperature coefficients, B_{ij} , of the DMSO oxygens became negative, which is physically meaningless.

Scattering factors and refinement conditions. The scattering factors used for all non-H atoms were calculated from analytical expressions for the neutral atoms.¹¹ For the H atoms the spherical form factors proposed by Stewart *et al.* were used.¹² Anomalous dispersion corrections were included for Hg, Cl and S.¹¹

The least-squares refinements were based on the minimization of $\sum w \|F_o\| - \|F_c\|^2$ and 2001 reflections with $F_o > 3.92 \sigma(F_o)$ were used. The weighting scheme used was $w = 1/[\sigma^2(F_o) + (0.04 F_o)^2]$ which,

according to a weight analysis, gave a satisfactory error distribution.

A total of 251 parameters, including one scale factor, was varied in the final refinements. The ratios of the shifts in the last cycle to the standard deviation were less than 0.1 in $P1$, except for the thermal parameters of the perchlorate oxygens, where the largest ratio was 0.4.

The final refined parameter values are given in Tables 1 and 2.

Table 1. Final fractional atomic positional parameters with estimated standard deviations in parentheses. The *G* values are the refined occupancy factors.

Atom	x	y	z	G
Hg	0.0	0.0	0.0	
Cl	0.7029(3)	0.6945(3)	0.3486(3)	
S1	0.2146(3)	0.3271(2)	0.1231(2)	
S2	0.3437(3)	-0.0243(3)	0.2147(2)	
S3	-0.1518(3)	0.1841(2)	0.3012(2)	
O1	0.0299(8)	0.2451(5)	0.0709(6)	
O2	0.2391(8)	0.0613(6)	0.1647(6)	
O3	-0.2016(8)	0.0540(6)	0.1651(6)	
O4	0.683(6)	0.661(3)	0.448(3)	0.74(7)
O5	0.747(8)	0.833(3)	0.441(5)	0.61(8)
O6	0.567(5)	0.690(9)	0.386(9)	0.53(10)
O7	0.848(5)	0.628(5)	0.321(5)	0.73(10)
O8	0.640(5)	0.573(3)	0.233(3)	0.74(6)
O9	0.834(6)	0.750(7)	0.312(5)	0.63(10)
O10	0.591(8)	0.758(6)	0.306(6)	0.57(8)
C1	0.2116(7)	0.4286(12)	0.3026(11)	
C2	0.2056(23)	0.4656(16)	0.0841(16)	
C3	0.4053(19)	-0.1725(17)	0.0698(16)	
C4	0.1796(21)	-0.1149(16)	0.2602(15)	
C5	-0.2192(18)	0.1400(15)	0.4258(12)	
C6	-0.3233(24)	0.3007(16)	0.3195(14)	
H1	0.219(12)	0.364(10)	0.345(9)	
H2	0.289(13)	0.496(10)	0.322(10)	
H3	0.108(13)	0.484(10)	0.313(10)	
H4	0.197(15)	0.431(11)	0.011(11)	
H5	0.104(13)	0.527(10)	0.144(10)	
H6	0.318(13)	0.522(10)	0.131(10)	
H7	0.298(13)	-0.221(10)	-0.002(10)	
H8	0.477(15)	-0.150(13)	0.060(13)	
H9	0.488(12)	-0.204(9)	0.144(10)	
H10	0.169(12)	-0.030(10)	0.359(10)	
H11	0.095(13)	-0.166(10)	0.184(10)	
H12	0.266(12)	-0.167(10)	0.288(10)	
H13	-0.130(14)	0.098(10)	0.440(10)	
H14	-0.140(12)	0.233(10)	0.526(10)	
H15	-0.311(14)	0.119(11)	0.414(11)	
H16	-0.311(12)	0.368(10)	0.410(10)	
H17	-0.472(12)	0.235(10)	0.264(10)	
H18	-0.284(14)	0.320(11)	0.277(11)	

Table 2. Final anisotropic thermal parameters ($\text{\AA}^2$) with estimated standard deviations in parentheses. The expression used is $\exp[-1/4B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots]$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	4.00(2)	2.79(2)	2.51(2)	0.21(1)	0.31(1)	0.92(1)
Cl	4.51(12)	5.33(12)	6.11(13)	-0.20(10)	0.30(10)	3.21(11)
S1	3.74(9)	3.54(9)	4.41(10)	0.19(7)	0.37(7)	1.69(8)
S2	4.89(10)	5.11(11)	4.16(10)	0.60(8)	-0.53(8)	2.26(9)
S3	4.97(10)	4.87(11)	3.09(9)	-0.63(8)	0.63(8)	1.22(8)
O1	4.7(3)	2.7(2)	3.9(3)	0.15(19)	-0.51(21)	0.60(20)
O2	5.7(3)	4.0(3)	4.5(3)	-0.02(23)	-1.68(24)	1.90(24)
O3	5.2(3)	4.6(3)	3.5(3)	-0.89(22)	1.13(22)	0.97(23)
O4	30.2(42)	19.6(24)	12.5(17)	3.2(24)	2.8(20)	13.1(17)
O5	28.4(50)	7.1(14)	18.1(37)	-4.3(18)	3.6(33)	-0.9(15)
O6	7.4(23)	37.2(94)	32.4(90)	-3.5(28)	11.6(34)	-4.8(60)
O7	12.7(23)	17.6(32)	39.4(61)	7.8(21)	9.8(29)	14.6(35)
O8	20.5(30)	15.5(22)	13.2(19)	-7.1(18)	-4.2(16)	7.2(16)
O9	13.2(27)	20.8(57)	23.7(45)	-6.8(28)	4.0(21)	11.1(39)
O10	25.2(57)	24.2(53)	28.0(54)	7.6(39)	-6.3(40)	19.8(47)
C1	6.2(6)	4.2(5)	4.8(5)	1.2(4)	0.0(4)	1.2(4)
C2	8.8(8)	6.4(7)	7.4(7)	-2.1(6)	-1.2(7)	4.3(7)
C3	6.0(7)	8.2(8)	6.1(6)	1.8(6)	1.4(6)	2.9(6)
C4	8.7(8)	7.9(7)	5.9(7)	1.5(6)	1.7(6)	4.4(6)
C5	5.7(5)	8.7(8)	4.9(5)	0.7(6)	0.9(5)	4.2(6)
C6	11.0(10)	6.5(7)	4.9(6)	1.6(7)	1.4(6)	2.7(5)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure is composed of discrete $\text{Hg}(\text{DMSO})_6^{2+}$ cations and ClO_4^- anions. Stereoscopic views of the molecular geometry of these ions are given in Figs. 1 and 2, and a unit cell view is

shown in Fig. 3. Some intramolecular distances and angles are given in Table 3.

The $\text{Hg}(\text{DMSO})_6^{2+}$ complex. Each Hg atom coordinates six DMSO molecules through the oxygen atoms. The resulting coordination polyhedron around the mercury(II) ion is a slightly distorted octahedron with an average Hg—O bond length

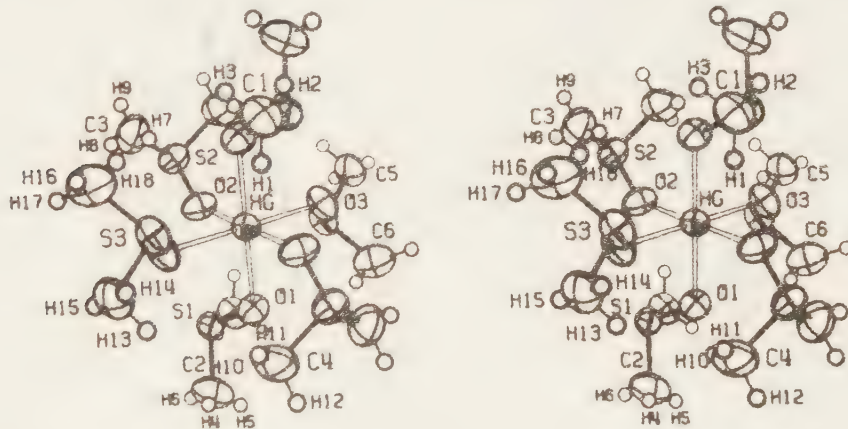


Fig. 1. A stereoscopic view of the centrosymmetrical $\text{Hg}(\text{DMSO})_6^{2+}$ cation. All non-H atoms are represented by 50% probability thermal ellipsoids. The H atoms have for clarity been given a B-value of $1 \text{ \AA}^2$ in the figure.

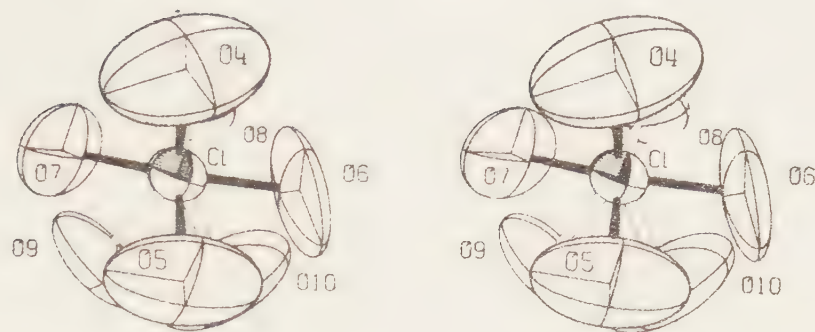


Fig. 2. A stereoscopic view of the disordered perchlorate ion. The thermal ellipsoids enclose 30% probability. The alternative oxygen positions are those with unfilled bonds.

of 2.34 Å. The sulfur atoms also form a somewhat irregular octahedron around mercury, with an average Hg–S distance of 3.41 Å.

The average S–O and S–C distances within the pyramidal DMSO molecules are 1.52 and 1.77 Å, respectively, which are in good agreement with distances found for other compounds with oxygen-coordinated DMSO ligands.^{13,14}

The C–H distances lie in the range 0.6 to 1.3 Å, the average value being 0.95 Å, close to values found by other X-ray diffraction determinations.^{15,17}

The ClO_4 ion. The seven oxygen positions O4 to O10 (Table 1) all belong to the perchlorate group (Fig. 2). The refined Cl–O distances are between 1.29 and 1.38 Å, except for Cl–O6 which is 1.12(5) Å. However, the corresponding distances for the oxygen peaks found from the Fourier difference map were all between 1.32 and 1.45 Å (Cl–O6 1.39 Å). The expected average Cl–O bond length should be 1.42–1.43 Å.¹⁶ The large deviations from expected values found for bond lengths and angles in the least-squares refinements are probably caused by the inadequate way of representing the librational

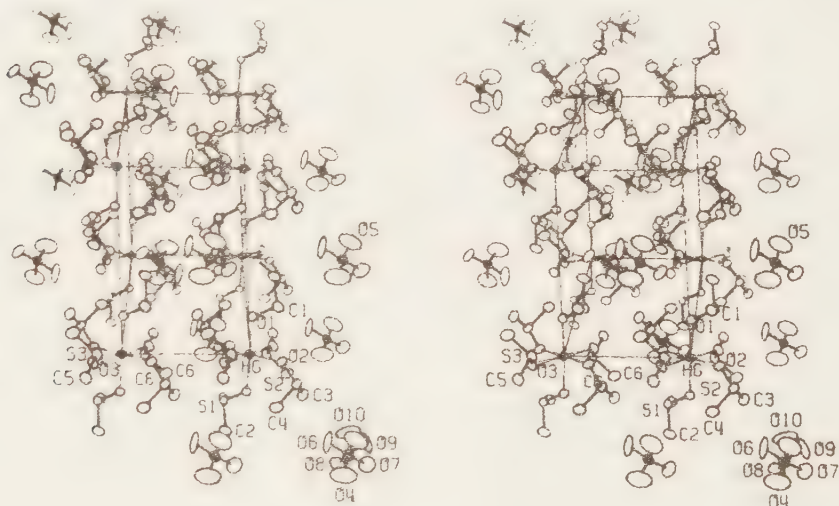


Fig. 3. A stereoscopic view along c^* of the triclinic unit cell. The a axis is horizontal in the figure. The thermal ellipsoids are drawn to enclose 30% probability. For clarity, the H atoms are omitted and only four of the seven oxygen positions are shown but for one of the disordered perchlorate groups.

Table 3. Some intramolecular atomic distances (Å) and angles (degrees) of interest. Estimated standard deviations are given in parentheses.

Hg—O1	2.376(6)	Cl—O4	1.34(3)
Hg—O2	2.320(6)	Cl—O5	1.37(4)
Hg—O3	2.317(6)	Cl—O6	1.12(5)
		Cl—O7	1.29(4)
Hg—S1	3.404(2)	Cl—O8	1.38(3)
Hg—S2	3.520(2)	Cl—O9	1.31(6)
Hg—S3	3.302(2)	Cl—O10	1.31(7)
Hg—C1	4.40(1)	O1—Hg—O2	82.4(2)
Hg—C2	4.82(2)	O1—Hg—O3	86.3(2)
Hg—C3	3.85(2)	O2—Hg—O3	89.6(2)
Hg—C4	3.88(2)	S1—Hg—S2	81.41(6)
Hg—C5	4.69(1)	S1—Hg—S3	75.71(6)
Hg—C6	4.45(2)	S2—Hg—S3	78.33(6)
		Hg—O1—S1	120.1(3)
S1—O1	1.522(6)	Hg—O2—S2	132.2(4)
S2—O2	1.513(7)	Hg—O3—S3	117.3(4)
S3—O3	1.518(7)	O1—S1—C1	106.2(5)
		O1—S1—C2	105.1(6)
S1—C1	1.78(1)	C1—S1—C2	97.9(7)
S1—C2	1.76(2)	O2—S2—C3	106.8(6)
S2—C3	1.76(2)	O2—S2—C4	106.0(6)
S2—C4	1.77(2)	C3—S2—C4	96.8(8)
S3—C5	1.77(2)	O3—S3—C5	106.2(6)
S3—C6	1.79(2)	O3—S3—C6	105.6(6)
		C5—S3—C6	96.7(7)

movements of the perchlorate oxygens by the ellipsoidal approximation. The thermal ellipsoids obtained for these oxygen atoms are also very large (Fig. 2). The distances were not corrected for thermal motion.

However, the residual electron density in the vicinity of the ClO_4^- group is between 0.5 and $-0.4 \text{ e } \text{\AA}^{-3}$ from a Fourier difference map. The sum of the refined occupancy factors of the seven oxygen positions is 4.55(23). This would mean that the refined model still accounts for the electron density of the perchlorate group to a fairly good extent.

The closest intermolecular approaches are O10—H9 2.16(12) and O5—H10 2.28(12) Å. In the absence of hydrogen bonds these intermolecular interactions will hardly cause any serious restraints on the librational movements of the perchlorate group.

Disordered perchlorate ions are also found in the structures of $\text{Ag}(\text{DMSO})_2\text{ClO}_4^{14}$ and $[\text{Cd}(\text{DMSO})_6]-(\text{ClO}_4)_2$.¹⁷ A survey of different types of disordered perchlorate ions is given in Ref. 14.

Acknowledgements. The authors wish to thank Dr. Georg Johansson and Prof. Sten Åhrland for valuable advice and interest in this work. The work has been financially supported by the Swedish Natural Science Research Council. A generous donation from the foundation Knut och Alice Wallenbergs Stiftelse to the departments of chemistry at the Royal Institute of Technology has made it possible to obtain the computer-controlled four-circle diffractometer with a complete program system for structure determinations.

REFERENCES

1. Gradenic, D. *Angew. Chem. Int. Ed. Engl.* 12 (1973) 435; Wells, A. F. *Structural Inorganic Chemistry*, Clarendon Press, Oxford 1975.
2. Kepert, D. L., Taylor, D. and White, A. H. *J. Chem. Soc. Dalton Trans.* (1973) 670.
3. Johansson, G. *Acta Chem. Scand.* 25 (1971) 2787.
4. Sandström, M., Persson, I. and Åhrland, S. *Acta Chem. Scand. A* 32 (1978). *In press.*
5. Johansson, G. and Sandström, M. *Acta Chem. Scand. A* 32 (1978) 109.
6. Sandström, M. *Acta Chem. Scand. A* 32 (1978). *In press.*
7. Kopfmann, G. and Huber, R. *Acta Crystallogr. A* 24 (1968) 348; North, A. C. T., Phillips, D. C. and Scott Mathews, F. *Ibid.* 351.
8. Syntex Analytical Instruments, Inc., 10040 Bubb Road, Cupertino, California 95014, USA.
9. Johnson, C. K. *A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL-5138, Oak Ridge National Laboratory, Oak Ridge 1976.
10. Åberg, M. *Acta Chem. Scand. A* 32 (1978) 101; Sundvall, B. *To be published.*
11. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4.
12. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
13. Biscarina, P., Fusina, L., Nivellini, G. D., Mangia, A. and Pelizzi, G. *J. Chem. Soc. Dalton Trans.* (1974) 1846.
14. Björk, N.-O. and Cassel, A. *Acta Chem. Scand. A* 30 (1976) 235.
15. Kvick, Å. *Aspects of Hydrogen Bonding in Biological Model Compounds*, *Acta Universitatis Upsaliensis*, Abstracts of Uppsala Dissertations from the Faculty of Science 322, Almqvist & Wiksell, Stockholm 1974.
16. Berglund, B., Thomas, J. O. and Tellgren, R. *Acta Crystallogr. B* 31 (1975) 1842.
17. Sandström, M. *Acta Chem. Scand. A* 32 (1978). *In press.*

Received August 26, 1977.

Acta Chem. Scand. A 32 (1978) No. 2

Received:

Other sheets: 6

Correspondence and proofs should be sent to

Fil.kand. Ingmar Persson, Oorganisk kemi 1, Kemicentrum,
Lunds Universitet, Box 740, S-220 07 Lund.

Running titles: Ahrland, Hansson, Iverfeldt and Persson

Mercury(II) Halide Complexes in DMSO

An X-Ray Diffraction and Raman Study of Mercury(II) Chloride,
Bromide and Iodide Complexes in Dimethylsulfoxide Solution.

STEN AHRLAND^a, EVA HANSSON^b, ÅKE IVERFELDT^c and INGMAR PERSSON^a.

^a Inorganic Chemistry 1, Chemical Center, University of Lund
P.O. Box 740, S-220 07 Lund 7, Sweden.

^b Physical Chemistry 1, Chemical Center, University of Lund,
P.O. Box 740, S-220 07 Lund 7, Sweden.

^c Department of Inorganic Chemistry, University of Gothenburg,
Chalmers Institute of Technology, S-412 96 Gothenburg, Sweden.

Dimethylsulfoxide solutions containing mercury(II) and halide in equimolar amounts have been investigated by raman and X-ray diffraction measurements. The complexes HgX^+ which are very stable in dilute solutions are found to disproportionate completely as the concentration increases. In the chloride and bromide systems, the simple reaction $2 \text{HgX}^+ \rightleftharpoons \text{Hg}^{2+} + \text{HgX}_2$ takes place. The complex HgCl^+ is completely disproportionated at $\underline{C}_M = 0.5 \text{ M}$, but at higher values of $\underline{C}_M$ the reaction is partly reversed. The complex HgBr^+ is completely disproportionated already at $\underline{C}_M = 0.1 \text{ M}$.

and remains so to saturated solution. In the iodide system, Hg^{2+} is not formed, but instead the dinuclear complex Hg_2I^{3+} most probably is, according to $3 \text{HgI}^+ \rightleftharpoons \text{Hg}_2\text{I}^{3+} + \text{HgI}_2$. This disproportionation is complete at $\underline{C}_M \approx 0.2 \text{ M}$ and is not reversed at higher values of $\underline{C}_M$. Evidently, the strong entropy stabilization which makes the species HgX^+ very prominent in dilute solutions completely disappears as $\underline{C}_M$ increases. The reason for this is discussed.

The structure of the tetrahedral complexes HgCl_4^{2-} and HgBr_4^{2-} finally formed as the halide concentration is increased have been determined by X-ray diffraction.

As in the protic solvent water, mercury(II) forms in the aprotic solvent dimethylsulfoxide (DMSO) a series of four mononuclear complexes HgX_j^{2-j} with chloride, bromide and iodide.^{1,2} Of the intermediate steps HgX^+ , HgX_2 and HgX_3^- , only the neutral complexes HgX_2 are very prominent in water.¹ In DMSO, on the other hand, all these steps are well separated in all the systems, at least at the mercury(II) concentrations covered by the stability measurements² ($\underline{C}_M \lesssim 20 \text{ mM}$). The maximum share of $\underline{C}_M$ reached by each complex (which occurs at the ligand number $\bar{n} = j$) is well over 90%, except for HgCl_3^- which, however, still exceeds 80%. The stabilization of the complexes HgX^+ in DMSO relative to water is exclusively an entropy effect.² Both enthalpy and entropy changes contribute, on the other hand, to the stabilization of the complexes HgX_3^- in DMSO.

Another striking difference between the two solvents is that the neutral complexes HgX_2 are all very soluble in DMSO,^{3,4} while in water their solubility varies⁵ from fair (HgCl_2) to very slight (HgI_2).

The fact that the mercury(II) halide complexes are so well separated in DMSO, in combination with their high solubility, makes it possible to determine their structures in solution by

X-ray diffraction technique. In water such measurements are possible only for the final complexes^{6,7} HgX_4^{2-} , and, to a certain extent,⁶ for HgBr_3^- and HgI_3^- . Studies recently performed in DMSO have also successfully elucidated the structures of all complexes HgX_2 , HgX_3^- and HgX_4^{2-} (except for HgCl_4^{2-} which was not investigated).^{3,4} In these measurements, the mercury(II) concentration has varied between 0.55 and 4.4 M, most solutions measured have been between 1 and 2 M. In all cases, the values of $\underline{C}_M$ have thus been about 100 times higher than in the stability measurements. In spite of this, however, the distribution between the complexes mentioned seem to be much the same as those found in the dilute solutions. For ligand concentrations $\underline{C}_L$ chosen so that $\underline{C}_L/\underline{C}_M = 2, 3$ and 4, the results of the diffraction studies are compatible with a strong predominance of the complexes HgX_2 , HgX_3^- and HgX_4^{2-} , respectively. To account for the radial distribution functions obtained, only one complex has to be introduced for each solution. The Hg-X bond distances calculated increase regularly in the order $\text{HgX}_2 < \text{HgX}_3^- < \text{HgX}_4^{2-}$, and the values are moreover close to those found for crystalline compounds containing these entities, Table 6. Evidently, the strength of the bonds Hg - X decreases as more ligands are coordinated.

The raman spectra of the solutions are also consistent with these results.⁴ For all the halides, the frequency of the prominent bond due to the Hg-X stretching mode(ν_1) decreases markedly in the order $\text{HgX}_2 > \text{HgX}_3^- > \text{HgX}_4^{2-}$, which directly indicates the weakening of the bond Hg - X accompanying the coordination of further ligands to the central ion.

The complexes HgX^+ , predominating at $\underline{C}_L/\underline{C}_M = 1$ in dilute solutions, behave in a manner very different to that of the higher complexes, however. At the values of $\underline{C}_M$ necessary for structure determinations, they have mainly disappeared, evidently due to disproportionation reactions.⁴ The large increase of the concentration would thus bring about very considerable changes of the relative stabilities of the complexes involved.

These changes were first indicated by the presence in the raman

spectra of concentrated solution⁴ with $\underline{C}_L/\underline{C}_M = 1$ of ν_1 (Hg - X) frequencies characteristic of the complexes HgX_2 . In the chloride and bromide systems the well-established Hg - O bending and stretching frequencies of the solvate⁸ $\text{Hg}(\text{DMSO})_6^{2+}$ were also found. In conformity with this, the bond lengths Hg - X calculated from X-ray diffraction studies of the solutions were close to those found for solutions with $\underline{C}_L/\underline{C}_M = 2$. Seemingly the same halide complexes HgX_2 predominated at both the ratios investigated.

The present investigation was undertaken primarily in order to study more closely the conditions prevailing in DMSO solutions containing halide and mercury(II) in the molar ratio 1:1. The first question is how the disproportionation depends upon the concentration in the various systems studied. In order to find an answer to this, raman spectra of 1:1 solutions of widely varying $\underline{C}_M$ have been recorded. Secondly, solutions of $\underline{C}_M = 0.8 \text{ M}$ have been studied by X-ray diffraction, and the results compared with those obtained previously⁴ for solutions of higher $\underline{C}_M$.

In addition, the structure of the complex HgCl_4^{2-} , missing in the earlier study, has been determined. Finally, a redetermination of the structure of HgBr_4^{2-} was undertaken, in order to ensure that the instrumental setup used in the present investigation yielded the same result as that used for the study of all the other mercury(II) halide complexes in DMSO solution.

EXPERIMENTAL

Preparation of solutions. The solutions were prepared by dissolving weighed amounts of mercury(II) halide (p.a.) and $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ or lithium halides (p.a.) in DMSO. The composition of the investigated solutions and of those investigated earlier are given in Table 1.

The solvate $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ was prepared and analyzed as described previously.⁸ The mercury(II) halides (p.a.) were recrystallized,⁹

and then carefully dried and stored in a vacuum desiccator at about 100°C. The lithium halides (p.a.) were recrystallized from water, dried and stored as the mercury(II) halides.

Raman measurements. The raman spectra were recorded, in the wavelength range 100 to 600 cm^{-1} , with a Cary 82 argon ion laser spectrophotometer using the 4880 Å line. Glass tubes with a diameter of 1 mm were used as sample holders for the solutions. The measurements were carried out at room temperature.

Diffraction measurements. The X-ray scattering from the free surface of the solution was measured in a θ - θ diffractometer of the same type as the one used by Johansson.^{6,10,11} The sample holder was a teflon container enclosed in an air-tight shield. MoK_α -radiation ($\lambda = 0.71069$ Å) was used with a lithium fluoride single crystal placed between the sample and the scintillation counter as monochromator. The amount of incoherently scattered radiation reaching the counter was estimated and checked as described before.³ The intensity of the diffracted radiation was measured at discrete points separated by 0.1° and 0.25° in the ranges $1^\circ \leq \theta \leq 30^\circ$ and $30 \leq \theta \leq 63^\circ$, respectively. For each point, 40000 counts were recorded twice. The data of Sandström used in this work are based on 100 000 counts per point. The corresponding statistical errors are 0.35% and 0.32%, respectively.

Treatment of diffraction data. The same data reduction procedure and corrections as described previously were applied.^{6,12} The experimental intensities were normalized to a stoichiometric unit of volume containing one mercury atom. The scattering factors, corrections for anomalous dispersion and values for incoherent scattering were the same as used before.⁶ The reduced intensity curves, $i_{\text{obs}}(\underline{s})$ multiplied by $\underline{s}$, where $\underline{s} = 4\pi\lambda^{-1}\sin \theta$, are given in Figs. 3 and 6. The corresponding electronic radial distribution functions (RDF), $\underline{D}(\underline{r}) - 4\pi\underline{r}^2\rho_0$, were obtained by Fourier transformation, Figs. 2 and 5. The same modification function as described previously was used.⁶ Spurious peaks below 1.5 Å which could not be related to interatomic distances within the DMSO molecule or the perchlorate ion have been removed by a Fourier

transformation procedure.¹⁰

All calculations were carried out on the UNIVAC 1100/80 computer of the University of Lund by means of the programs KURVLR and PUTSLR.¹²

RAMAN MEASUREMENTS

Raman spectra have been recorded for solutions of $\underline{C}_L/\underline{C}_M = 1$, with $\underline{C}_M$ varying from 0.035 M to saturation which is reached at $\underline{C}_M = 1.3, 1.5$ and 1.3 M for chloride, bromide and iodide, respectively.⁴ The $\nu_L(\text{Hg} - \text{X})$ bands were found at 303, 195 and 145 cm^{-1} , i.e. at the wavenumbers reported by Sandström⁴ both for solutions of HgX_2 ($\underline{C}_L/\underline{C}_M = 2$) and for solutions of the present ratio $\underline{C}_L/\underline{C}_M = 1$. The chloride and bromide spectra show the bending and stretching $\text{Hg} - \text{O}$ frequencies at 200 and 425 cm^{-1} which are characteristic⁶ for the solvate $\text{Hg}(\text{DMSO})_6^{2+}$. In the iodide spectra, these bands are absent, but a relatively sharp band at 173 cm^{-1} appears instead. In concentrated aqueous solutions ($2 \text{ M} \leq \underline{C}_M \leq 4 \text{ M}$) an analogous band has been found, at 168 cm^{-1} , which has been assigned to the dinuclear complex¹⁴ Hg_2I^{3+} . Very plausibly such a complex also exists in DMSO. If so, it should be especially prominent in concentrated solutions containing a large excess of mercury(II). In fact, in the raman spectrum of a solution of $\underline{C}_M = 1 \text{ M}$ and $\underline{C}_D/\underline{C}_M = 0.4$, the peak related to Hg_2I^{3+} persists, while that of HgI_2 disappears almost completely.¹⁵ No bands that can be assigned to HgX^+ were found in any of the investigated solutions.

The disproportionation of HgCl^+ and HgBr^+ in concentrated DMSO solutions thus seems to occur according to the simple mononuclear reaction $2 \text{HgX}(\text{DMSO})_6^+ + n \text{DMSO} \rightleftharpoons \text{HgX}_2(\text{DMSO})_q + \text{Hg}(\text{DMSO})_6^{2+}$ with the equilibrium constant

$$K_{\text{HgX}} \cdot [\text{DMSO}]^n = \frac{[\text{HgX}_2][\text{Hg}(\text{DMSO})_6^{2+}]}{[\text{HgX}^+]^2} \quad (1)$$

while the disproportionation of HgI^+ most probably occurs according to



with the equilibrium constant

$$K_{\text{HgI}} \cdot [\text{DMSO}]^n = \frac{[\text{HgI}_2][\text{Hg}_2\text{I}^{3+}]}{[\text{HgI}^+]^3} \quad (2)$$

To determine how far the disproportionation has proceeded at a certain C_M , the ratio h/C_M is formed where h is the height of the $\nu_1(\text{Hg} - \text{X})$ peak (in arbitrary units). As h is proportional to $[\text{HgX}_2]$, this ratio is proportional to $[\text{HgX}_2]/C_M$. For this quantity, the following expressions can be deduced from eq.(1) and (2), referring to chloride and bromide (1a), and to iodide (2a):

$$\frac{[\text{HgX}_2]}{C_M} = \frac{1}{(K_{\text{HgX}} \cdot [\text{DMSO}]^n)^{-1/2} + 2} \quad (1a)$$

$$\frac{[\text{HgI}_2]}{C_M} = \frac{1}{([\text{HgI}_2] \cdot K_{\text{HgI}} \cdot [\text{DMSO}]^n)^{-1/3} + 3}$$

As expressed by eq. (1a), a simple disproportionation of the type (1) should per se be independent of C_M . From the ratios h/C_M plotted in Fig. 1a,b it is obvious that this is not the case. As already found in the stability measurements,² no disproportionation occurs at low C_M . With increasing C_M , however, the disproportionation rather suddenly becomes prominent. In the case of chloride, h/C_M slowly decreases after having passed a maximum, Fig. 1a. In the case of bromide, on the other hand, the high value of h/C_M reached stays constant as C_M is further increased, Fig. 1b.

The maximum value of h/C_M reached at $C_M \approx 0.5 \text{ M}$ in the chloride

system is the same as obtained for a 0.25 M solution of HgCl_2 , i.e. exactly the value expected for a complete disproportionation according to eq. (1). The following partial reproporationation must be due to a decrease of $K_{\text{HgX}}[\text{DMSO}]^n$. Since both K_{HgX} and n presumably vary with C_M and, moreover, $[\text{DMSO}]$ cannot possibly be calculated, it seems fruitless to speculate about the reasons for this decrease. To judge from the relative intensities, about 1/3 of the total mercury ought to be present as HgCl_2 in saturated solution, as against 1/2 when the disproportionation is complete, at $C_M = 0.5$ M.

The constant value of h/C_M found for $C_M \gtrsim 0.1$ M in the bromide system per se strongly suggests that complete disproportionation takes place in this region. That this is indeed the case has been proved by measuring the value of h/C_M for a 0.25 M solution of HgBr_2 . This value is twice as large as that of the plateau in Fig. 1b, just as expected if within the whole of this region a complete disproportionation takes place according to eq. (1).

In the case of the more complicated disproportionation proposed for the iodide system, $[\text{HgI}_2]/C_M$, and hence h/C_M , should depend upon C_M until $([\text{HgI}_2]K_{\text{HgI}}[\text{DMSO}]^n)^{-1/3} \ll 3$, cf. eq. (2a). When this condition is met, $[\text{HgI}_2]/C_M = 1/3$, i.e. a disproportionation taking place according to eq. (2) is then complete. The constant value of h/C_M found for $C_M \gtrsim 0.2$ M, Fig. 1c, thus strongly indicates that the disproportionation is complete in this region. The final proof is the fact that an 1 M HgI_2 solution has a value of h/C_M three times higher than that of the plateau in Fig. 1c, i.e. just as expected if the disproportionation takes place according to eq. (2).

The addition of even large amounts of ammonium perchlorate, used to provide an ionic medium in the stability measurements, does not influence the disproportionation of HgI^+ . Thus solutions of $0.1 \text{ M} \leq C_M \leq 0.3 \text{ M}$, containing ammonium perchlorate to a total ionic strength of 1.2 M, have the same raman spectra as solutions with no salt added.

The accuracy in the determination of the peak intensities is lower for HgCl_2 than for HgBr_2 and HgI_2 , as the ν_1 (Hg - Cl) band of HgCl_2 cannot be resolved from one of the bands related to DMSO.⁴ The contribution from the DMSO peak was estimated from the intensities of undisturbed DMSO peaks in the same spectrum.

X-RAY DIFFRACTION MEASUREMENTS

Pure DMSO. In the present diffraction measurements, the values of C_M were lower than previously, and more precise corrections for the contributions from DMSO were needed. The data previously recorded for pure DMSO have therefore been refined.

The RDF function for pure DMSO has a peak at about 1.8 Å and a marked shoulder at about 1.5 Å, corresponding to S-C and S-O bond distances, respectively. A prominent shoulder at about 2.7 Å corresponds to the O-C and C-C interactions, Fig 2. The very broad peaks at about 5.5 and 10 Å are probably due to interactions between DMSO molecules. The final parameters from the refinements of the reduced intensity curve, Fig. 3, are given in Table 2.

The intramolecular distances determined for liquid DMSO agree very well with those found for this compound in solid¹⁶ and gaseous¹⁷ state. One investigation¹⁸ of the solid at +5°C differs markedly from the other results, however, which may be due to the fact that the investigation has been performed not far from the melting point where the thermal movements are large. The intramolecular bond distances and angles in the three states of aggregation are given in Table 3.

Formal HgXClO_4 solutions. The disproportionation of the HgX^+ complexes results in three or, when the disproportionation is complete, two different mercury(II) species in the solution. Even in the latter case, however, the concentration of each complex is too low to permit any refinement of the individual d , b and n parameters, see Table 2.

In Hg^{2+} , HgCl_2 and HgBr_2 all these parameters are known from measurements on solutions where these species completely predominate.^{4,6} In HgI_2 , the parameters referring to the Hg-I distance are well known, but not those referring to the solvation. In the case of Hg_2I^{3+} , finally, no parameters have so far been measured. For the present calculations, the unknown parameters have been estimated as described below.

For the chloride and bromide solutions the known parameters of the disproportionation products^{4,8} $\text{Hg}(\text{DMSO})_6^{2+}$ and HgX_2 have been used in the calculations of theoretical radial distribution functions and intensity curves assuming complete disproportionation. The differences $(D(r)_{\text{obs}} - D(r)_{\text{calc}})$ are smooth and have about the same shape as for pure DMSO, Fig 2. The $\underline{s}_{\text{obs}}(s)$ and $\underline{s}_{\text{calc}}(s)$ functions agree well both for the two bromide solutions and for the solution HgCl , Fig 3. For HgClMS , however, a marked shoulder at about 2.3 Å in the difference RDF indicates a less fortunate choice of the Hg-Cl and Hg-O parameters.

Least square refinements of $\underline{d}$ and $\underline{b}$ results for both the bromide solutions in values which are, within the limits of error, the same as those found for the HgBr_2 complex,⁴ Table 4. The corresponding results for the Hg-Cl interactions differ significantly. The value of $\underline{d}$ obtained from the HgCl solution is very close to that found in HgCl_2 , while the value found⁴ from HgClMS is markedly shorter, Table 4.

In the RDF's of the iodide solutions, Fig 2, the intense peak at about 2.6 Å corresponds to Hg-I interactions. The sharpness of this peak indicates that the Hg-I distances of the assumed complexes HgI_2 and Hg_2I^{3+} must be almost identical. The shoulder in the RDF's at about 3.7 Å is very likely due to the Hg-Hg interaction in Hg_2I^{3+} and also to Hg-S interactions involving coordinated DMSO. With a Hg-I distance of 2.6 Å, an angle Hg-I-Hg in Hg_2I^{3+} of about 90° is found. This fits nicely with the fact that endless chains in the compound $(\text{HgI})_2\text{TiF}_6$ in solid state have Hg-I distances of 2.62 Å and Hg-I-Hg angles close to 90° .¹⁹

For steric reasons not more than three DMSO can be coordinated to each mercury atom in Hg_2I^{3+} , as is evident from a molecular model. With the type of disproportionation assumed for HgI^+ , this means that the corresponding Hg-O and Hg-S interactions have frequency factors $\bar{n} \leq 2$ when referred to the total mercury(II) concentration. The estimated parameters used to describe these interactions are given in Table 4B. The average Hg-O and Hg-S distances are assumed to be somewhat shorter than in $\text{Hg}(\text{DMSO})_6^{2+}$ and because of the less regular coordination the temperature factors are given somewhat larger values than found for $\text{Hg}(\text{DMSO})_6^{2+}$. As illustrated in Fig 4a, the $\underline{si}(s)$ functions calculated for these interactions are less than the experimental errors in the region $\underline{s} \gtrsim 5 \text{ \AA}^{-1}$.

According to a recent raman investigation, two DMSO molecules are coordinated to HgI_2 in DMSO solution.²⁰ If so, the frequency factors of the Hg-O and Hg-S interactions of HgI_2 are 0.67 in the present solutions, where only 1/3 of the mercury is present as HgI_2 . Judging from the data found for HgCl_2 and HgBr_2 , Table 4B, the Hg-O and Hg-S distances are probably about 2.6 and 3.7 Å, respectively, and the $\underline{b}$ parameters around $0.03 \text{ \AA}^2$.

With these models for the solvation of HgI_2 and Hg_2I^{3+} , the parameters $\underline{d}$ and $\underline{b}$ of the Hg-I and Hg-Hg interactions were refined, Table 4A. Between the different $\underline{s}$ ranges refined, the Hg-I parameters are constant within $\pm 0.01 \text{ \AA}$ and $0.001 \text{ \AA}^2$ for $\underline{d}$ and $\underline{b}$, respectively. The variations are thus somewhat larger than the standard deviations. No significant differences in the parameters are found between the two iodide solutions studied.

It was not possible to obtain any reliable values of the Hg-Hg parameters by least squares refinements. This means that $\underline{b}$ is $\gtrsim 0.02 \text{ \AA}$, Fig 4b. A good fit with the RDF is obtained for $\underline{d}_{\text{Hg-Hg}} = 3.70$ and $\underline{b}_{\text{Hg-Hg}} = 0.03 \text{ \AA}^2$, Fig 2. As seen in Fig 4c, the contribution of these parameter values to $\underline{si}_{\text{obs}}(\underline{s})$ is negligible for $\underline{s} \gtrsim 5 \text{ \AA}^{-1}$. The value $\underline{b}_{\text{Hg-Hg}}$ corresponds to a root mean square variation of $0.24 \text{ \AA}$ in the average Hg-Hg distance, which in turn corresponds to a variation of $\pm 6^\circ$ in the angle Hg-I-Hg. This is a

reasonable flexibility in view of the fact that the Hg-I-Hg angles in the endless chains¹⁹ of $(\text{HgI})_2\text{TiF}_6(\text{s})$ are 89° and 97° .

The satisfactory fit of the model adopted with the actual data is evident from Figs 2 and 3.

HgX_4^{2-} solutions. To judge from the stability measurements, the predominating species in the solutions HGCL4 and HGBR4 are HgCl_4^{2-} and HgBr_4^{2-} , respectively. That this is really the case is confirmed by the raman spectra. The $\nu_1(\text{Hg-X})$ bands are found just at the wavenumbers expected, 200 cm^{-1} for HgCl_4^{2-} and 160 cm^{-1} for HgBr_4^{2-} , and no band exist that can be assigned to lower complexes.

Besides the usual peaks due to interactions within DMSO, and between DMSO molecules, only two peaks, or shoulders, are present in the RDF's, Fig 5. The intense peaks at $\approx 2.5\text{ \AA}$ in HGCL4 and $\approx 2.6\text{ \AA}$ in HGBR4 correspond to Hg-X bond distances. The diffuse shoulder at $\approx 4\text{ \AA}$ in HGCL4 and the small peak at $\approx 4.3\text{ \AA}$ in HGBR4 correspond to X-X distances in the tetrahedral complexes. The refined parameters are given in Table 5, and the good fit is demonstrated in Fig 6.

The Hg-X and X-X distances obtained, Table 5, show beyond doubt that the complexes HgCl_4^{2-} and HgBr_4^{2-} are regular tetrahedrons. The ratios $\frac{d_{\text{Hg-X}}}{d_{\text{X-X}}}$ found are 0.612(7) and 0.612(2), respectively, i.e. very close to the expected tetrahedral value of 0.6124. The number of Hg-X and X-X distances obtained are also consistent with this structure. The distances and angles of HgBr_4^{2-} found agree well with those previously reported.⁴

CONCLUSIONS

The disproportionation reactions inferred from the raman data of solutions containing mercury(II) and halide in equimolar amounts are compatible with the results of the diffraction measurements.

For chloride and bromide, the reaction thus occurs according to eq. (1), for iodide according to eq. (2), with the formation of a dinuclear complex. For chloride, the disproportionation is seemingly partly reversed at high values of $\underline{C}_M$, for bromide and iodide it stays complete up to saturated solution.

In the potentiometric and calorimetric measurements² where $\underline{C}_M \leq 20$ mM, the number of DMSO per mercury is always very large, Fig. 1d. Under these conditions, HgX^+ is, as mentioned earlier, exceptionally stable towards disproportionation. Such reactions begin as $\underline{C}_{\text{DMSO}}/\underline{C}_M$ decreases, and the disproportionation is complete for the approximate ratios 30, 150 and 75 for chloride, bromide and iodide, respectively. Evidently these changes are enough to destroy that entropy stabilization which renders the complex HgX^+ so very stable. This would mean that once $\underline{C}_{\text{DMSO}}/\underline{C}_M$ are down to these values, a really unstructured bulk solvent no longer exists. It is not easy to rationalize however, why the disproportionation becomes prominent at such different values of $\underline{C}_{\text{DMSO}}/\underline{C}_M$ for the various halides. The easy formation of dimers, and generally polymers in iodide solutions, as compared with chloride or bromide solutions, is well known.

On the other hand, it is rather surprising that the ordering effect exerted by ammonium ions does not affect the degree of disproportionation.

In all the complexes HgX_n^{2-n} , $\underline{n} = 2-4$, the bonds Hg-X are somewhat longer in DMSO than in water, Table 6. This lengthening indicates that the neutral and anionic mercury halide complexes are more strongly solvated by DMSO than by water. In conformity with this, the bonds Hg-X are generally even shorter in solids compounds containing these complexes, Table 6.

In solutions of Hg^{2+} , where the length of the solvate bond Hg-O can be directly measured,⁸ the distance seems to be much the same in $\text{Hg}(\text{DMSO})_6^{2+}$ and in $\text{Hg}(\text{H}_2\text{O})_6^{2+}$, viz. 2.39 - 2.40 Å. In these two solvates, the bonds are therefore of about the same strength.

ACKNOWLEDGEMENTS

Our thanks are due to Dr. Magnus Sandström for making his experimental diffraction data available to us. The continued interest of Professor Oliver Lindqvist has greatly facilitated our work. We are further indebted to Professor Kåre Larsson, for putting the raman spectrophotometer at our disposition. We gratefully acknowledge the support given to these investigations by The Swedish Natural Science Research Council.

REFERENCES

1. Sillén, L.G. Acta Chem. Scand. 3 (1949) 539.
2. Åhrland, S., Persson, I. and Portanova, R. To be published.
3. Gaizer, F. and Johansson, G. Acta Chem. Scand. 22 (1968) 3013.
4. Sandström, M. Acta Chem. Scand. A32 (1978) 627.
5. Handbook of Chemistry and Physics, CRC Press, Cleveland, 58 th Ed., 1977-1978.
6. Sandström, M. and Johansson, G. Acta Chem. Scand. A31 (1977) 132.
7. Sandström, M. Acta Chem. Scand. A31 (1977) 141.
8. Sandström, M., Persson, I. and Åhrland, S. Acta Chem. Scand. A32 (1978) 607.
9. Åhrland, S., Kullberg, L. and Portanova, R. Acta Chem. Scand. A32 (1978) 251.
10. Levy, H.A., Danford, M.D. and Narten, A.H. Data Collection and Evaluation with X-Ray Diffractometer Designed for the Study of Liquid Structure, Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge 1966.
11. Johansson, G. Acta Chem. Scand. 20 (1966) 553.
12. Sandström, M. Diss., Royal Institute of Technology, Stockholm 1978.
13. Johansson, G. and Sandström, M. Chem. Scr. 4 (1973) 195.
14. Clarke, J.H.R. and Woodward, L.A. Trans. Faraday Soc. 61 (1965) 207.
15. Holmberg, B., Iverfeldt, Å. and Persson, I. To be published.
16. Viswamitara, M.A. and Kannan, K.K. Nature 209 (1966) 1016.
17. Bastiansen, O. and Viervoll, H. Acta Chem. Scand. 2 (1948) 702

18. Thomas, R., Brink Shoemaker, C. and Eriks, K. Acta Crystallogr. 21 (1966) 12.
19. Köhler, K., Breitinger, D. and Thiele, G. Angew. Chem. Int. Ed. England 13 (1974) 821.
20. Joly, J.P. and Nicolau, I.F. Spectrochim. Acta 35A (1979) 281.
21. Stålhandske, C.I. Personal communication.
22. Sandström, M. and Liem, D.H. Acta Chem. Scand. A32 (1978) 509.
23. Ferguson, G., Jeffreys, J.A.D. and Sim, G.A. J. Chem. Soc. B (1966) 454.
24. Clegg, W., Brown, M.L. and Wilson, L.J.A. Acta Crystallogr. B32 (1976) 2905.
25. Leligny, H., Frey, M. and Monier, J.C. Acta Crystallogr. B28 (1972) 2104.
26. White, J.G. Acta Crystallogr. 16 (1963) 397.
27. Kamenar, B. and Nagl, A. Acta Crystallogr. B32 (1976) 1414.
28. Jeffrey, G.A. and Vlasse, M. Inorg. Chem. 6 (1967) 396.
29. Gerken, V.A. and Pakhomov, V.I. Zh. Strukt. Khimii 10 (1969) 753.
30. Pakhomov, V.I., Fedorov, P.M., Alynov, I.M., Ivanova-Korfini, I.N. and Semin, G.K. Ives. Akad. Nauk. SSSR Ser. Fiz. 39 (1975) 2519

Table 1. Concentrations/M of the solutions investigated by X-ray diffraction. The linear absorption coefficient μ/cm^{-1} is calculated for MoK_α -radiation.

Solution	Hg(II)	X ⁻	ClO_4^-	Li	DMSO	μ
HGCL	0.80	0.80	0.80		13.0	24.0
HGCLMS	1.30	1.30	1.30		13.0	35.5
HGCL4	0.40	1.80		1.00	13.6	14.8
HGBR	0.80	0.80	0.80		13.1	27.8
HGBRMS	1.54	1.47	1.61		12.3	49.2
HGBR4	0.40	1.80		1.00	13.8	22.8
HGI	0.80	0.80	0.80		13.4	27.5
HGIMS	1.27	1.27	1.27		12.7	39.9
Pure DMSO					14.0	4.9

Table 2. Least-squares refinements on the reduced intensities for pure DMSO. The refined parameters $\underline{d}$ = distance ($\text{\AA}$), $\underline{b}$ = temperature factor coefficient ($\text{\AA}^2$) and $\underline{n}$ = number of distances per sulfur atom are obtained for the range $5.5 \leq \underline{s} \leq 16 \text{\AA}^{-1}$ of the reduced intensity curve. The refined parameters are given within paranthesis.

Interaction	S - O	S - C	O - C	C - C
$\underline{d}$	1.496(4)	1.805(4)	2.661(8)	2.774(10)
$\underline{b}$	0.0006(5)	0.0020(3)	0.000(1)	0.0006(2)
$\underline{n}$	1.0	2.0	2.0	1.0

Table 3. Interatomic distances (Å) and angles (degrees)
in gaseous, liquid and solid DMSO.

	Gaseous ¹⁷	Liquid ^a	Solid ¹⁶
S - O distance	1.47	1.496(4)	1.471(8)
S - C distance	1.82	1.805(4)	1.812(14) 1.801(10)
C - S - O angle	107(5)	107.0(9)	107.0(6) 107.4(5)
C - S - C angle	100(5)	100.4(8)	97.9(5)

a This work.

Table 4. Parameters for the solvated mercury(II) complexes formed in solutions of $\underline{C}_L/\underline{C}_M = 1$.

A: Results of the least-squares refinements obtained for the range $6 \leq \underline{s} \leq 16 \text{ \AA}^{-1}$ of the $\underline{si}_{\text{exp}}(\underline{s})$ curves. About symbols and standard deviations, see Table 2. $\underline{n}$ =number of distances per mercury atom.

Interaction	<u>d</u>	<u>b</u>	<u>n</u>	Solution
Hg - I	2.621(2)	0.0053(2)	1.33	HGIMS
	2.607(2)	0.0058(3)	1.33	HGI
Hg - Br	2.455(3)	0.0021(2)	1.0	HGBRMS
	2.469(4)	0.0032(5)	1.0	HGBR
Hg - Cl	2.300(3)	0.0018(5)	1.0	HGCLMS
	2.363(6)	0.0014(7)	1.0	HGCL

B: The parameters used in the calculations of the RDF and $\underline{si}_{\text{calc}}(\underline{s})$ curves. In addition, parameters for DMSO were taken from Table 2 and for ClO_4^- from Ref 4.

Interaction	<u>d</u>	<u>b</u>	<u>n</u>	Complex	Ref
Hg - I	2.615	0.006	1.33	$\text{HgI}_2 + \text{Hg}_2\text{I}^{3+}$	this work
Hg - Hg	3.70	0.030	0.33	$\text{Hg}_2\text{I}(\text{DMSO})_6^{3+}$	- " -
Hg - O	2.35	0.015	2	- " -	- " -
Hg - S	3.35	0.025	2	- " -	- " -
Hg - Br	2.452	0.0015	1	$\text{HgBr}_2(\text{DMSO})_4$	4
Hg - O	2.64	0.031	2	- " -	4
Hg - S	3.57	0.029	2	- " -	4
Hg - Cl	2.350	0.0013	1	$\text{HgCl}_2(\text{DMSO})_4$	4
Hg - O	2.53	0.021	2	- " -	4
Hg - S	3.68	0.043	2	- " -	4
Hg - O	2.393	0.0108	3	$\text{Hg}(\text{DMSO})_6^{2+}$	8
Hg - S	3.427	0.0194	3	- " -	8

Table 5. Least-squares refinements on the reduced intensities for DMSO solutions of HgCl_4^{2-} and HgBr_4^{2-} . In the case of HgBr_4^{2-} , data from an earlier study are also listed. About symbols and standard deviations, see Table 2; $\underline{n}$ = number of distances per mercury atom.

Interaction	Parameter	$\text{HgCl}_4^{\underline{a}}$	$\text{HGBR}_4^{\underline{a}}$	HgBr_4^{2-4}
Hg - X	$\underline{d}$	2.532(2)	2.628(3)	2.628(2)
	$\underline{b}$	0.0013(4)	0.0076(2)	0.0058(4)
	$\underline{n}$	3.7(1)	4.0(1)	4.1(2)
X - X	$\underline{d}$	4.14(4)	4.293(13)	4.31(1)
	$\underline{b}$	0.025(6)	0.0152(4)	0.026(8)
	$\underline{n}$	6.0	6.0	6(2)

$\underline{a}$ This work.

Table 6. Distances Hg - X (Å) in HgX_2 , HgX_3^- and HgX_4^{2-} ,
 X = Cl, Br and I, in DMSO solution and in solid phases;
 for HgX_4^{2-} also aqueous solution.

		HgX_2	HgX_3^-	HgX_4^{2-}
Cl	solid	2.280(7) ²¹	2.432(3) ²²	2.495(10) ²³ , 2.464(1) ²⁴
	DMSO	2.350(3) ⁴	2.434(3) ⁴	2.532(2) ^a
	aq			2.47(11) ¹¹
Br	solid	2.424(5) ²⁵	2.48(3)-2.56(3) ²⁶	2.488(4) ²⁷
	DMSO	2.455(2) ⁴	2.547(3) ⁴	2.628(2) ^{a,4}
	aq			2.610(5) ⁶
I	solid	2.618(6) ²⁸	2.72(1) ²⁹	2.77(1) ³⁰ , 2.783(3) ²⁸
	DMSO	2.624(8) ⁴	2.733(3) ³	2.796(3) ³
	aq			2.785(3) ⁶

a This work.

Fig. 1. a-c. Ratios $\underline{h}/\underline{C}_M$ between the peak heights of the $\underline{\nu}_1$ (Hg - X) bands of the HgX_2 complexes formed by disproportionation in solutions of $\underline{C}_L/\underline{C}_M = 1$, and the total mercury(II) concentration. The values of $\underline{h}/\underline{C}_M$ are on an arbitrary scale. The figures refer to the chloride (a), bromide (b) and iodide (c) solutions, measured at 303, 195 and 145 cm^{-1} , respectively.

Fig. 1 d. Number of DMSO per mercury atom as a function of $\underline{C}_M$.

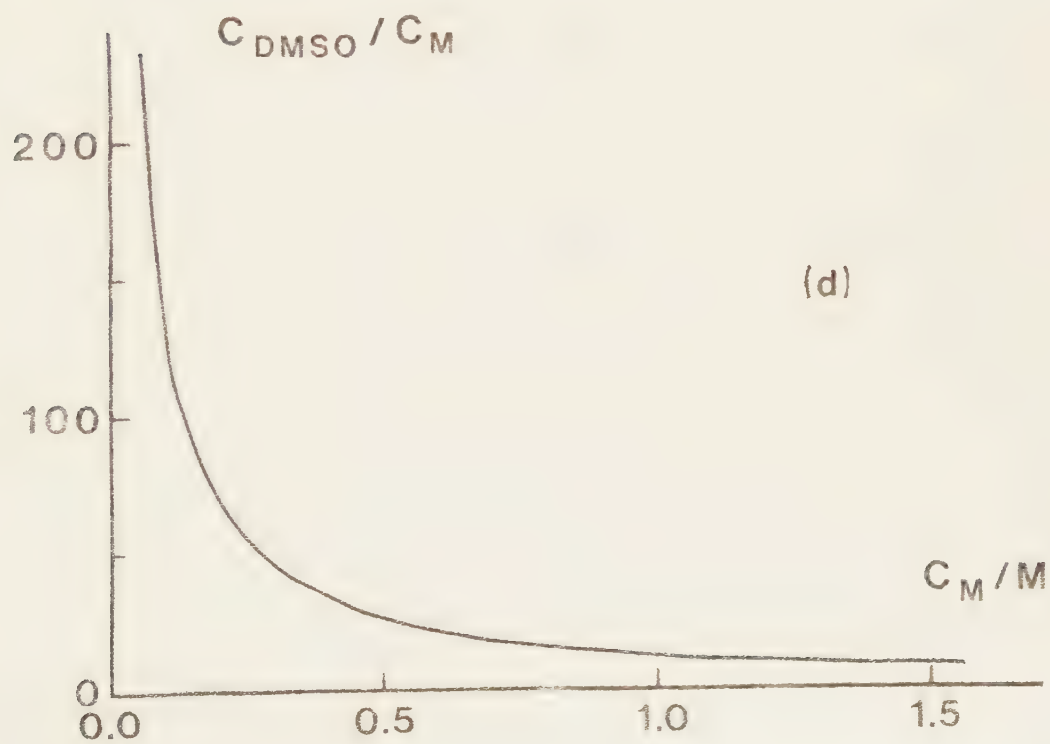
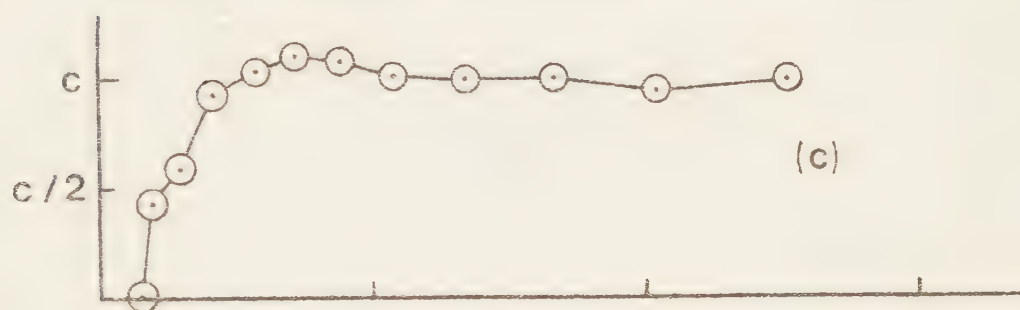
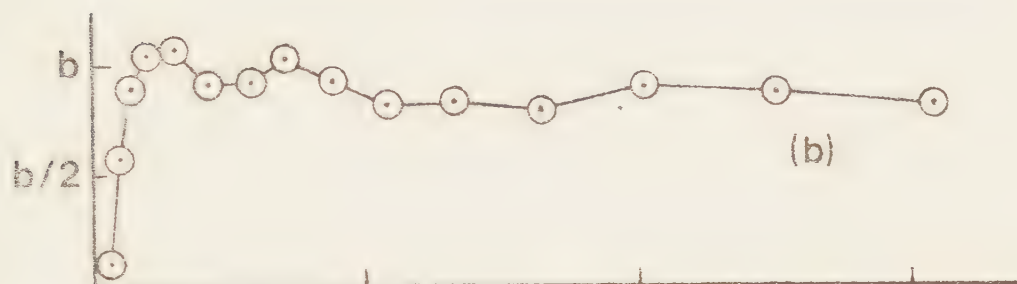
Fig. 2. $\underline{D}(\underline{r}) - 4\pi r^2 \rho_O$ functions of the solutions of $\underline{C}_L/\underline{C}_M = 1$ (solid lines) compared with sums of calculated peak shapes (dashed lines). The differences are shown by dashed-dotted lines.

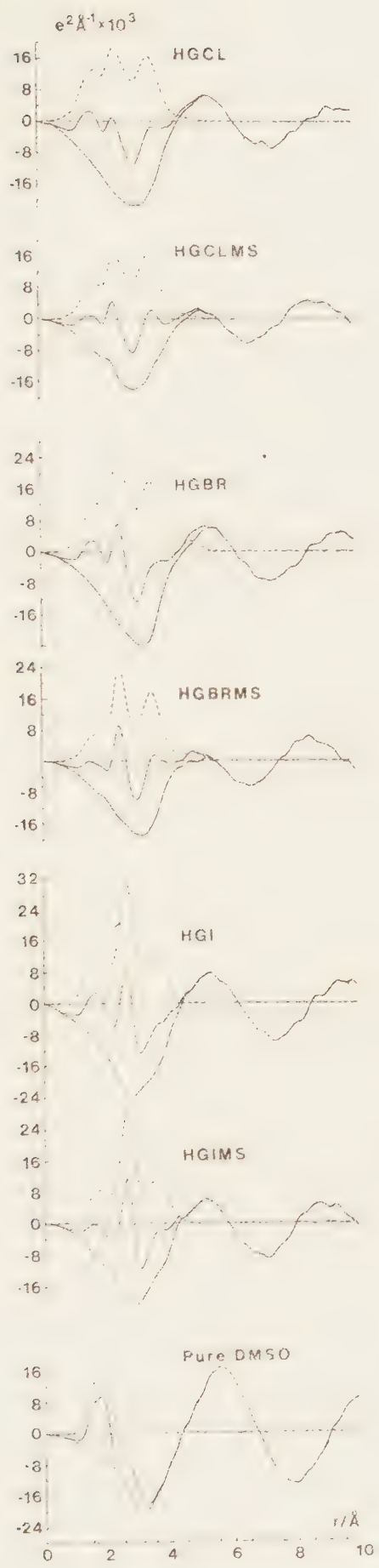
Fig. 3. Reduced intensities multiplied by $\underline{s}$ for pure DMSO and for the solutions of $\underline{C}_L/\underline{C}_M = 1$ investigated. Experimental values are denoted by dots. Values calculated for the refined model (with the parameter values of Table 2 and 4) are represented by solid lines, to the left, differences between experimental and calculated values by dots to the right.

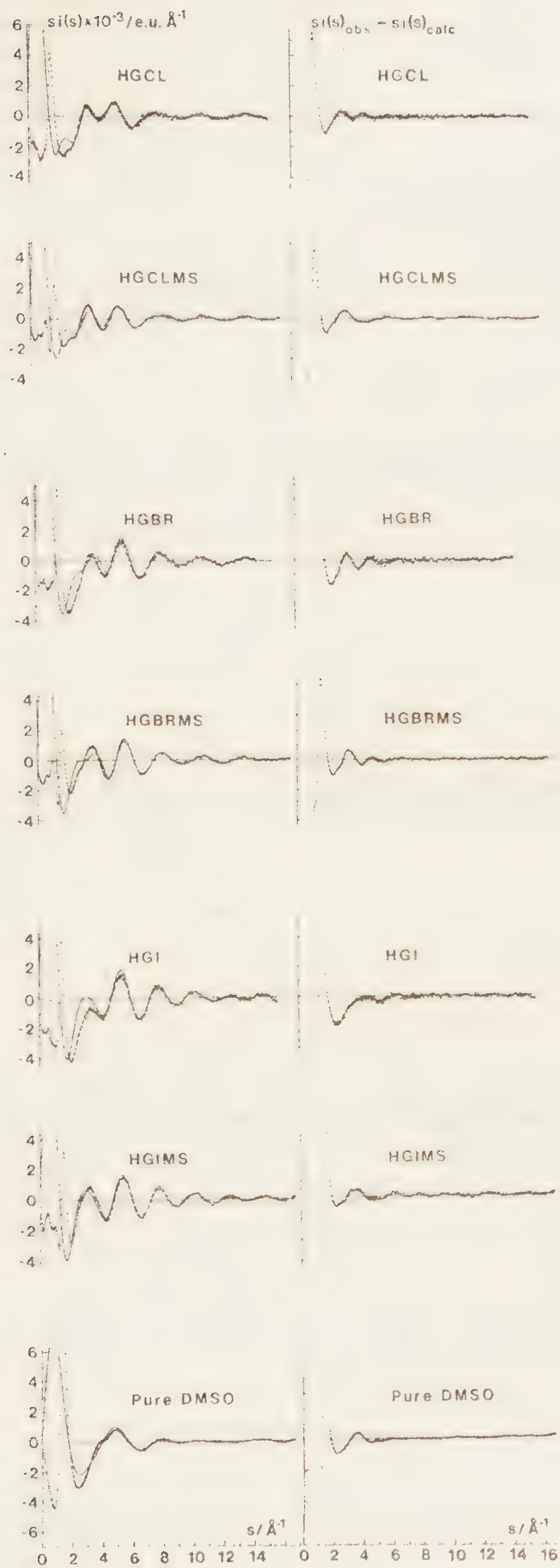
Fig. 4. The calculated contribution (solid lines) to the function $\underline{s}_i(\underline{s})$ of the HGIMS solution from a Hg - S interaction with $\underline{d} = 3.35 \text{ \AA}$, $\underline{b} = 0.025 \text{ \AA}^2$ and $\underline{n} = 2$ (a) a Hg - Hg interaction with $\underline{d} = 3.70 \text{ \AA}$, $\underline{b} = 0.02 \text{ \AA}^2$ and $\underline{n} = 0.33$ (b); and by the same Hg - Hg interaction with $\underline{b} = 0.03 \text{ \AA}^2$ (c).

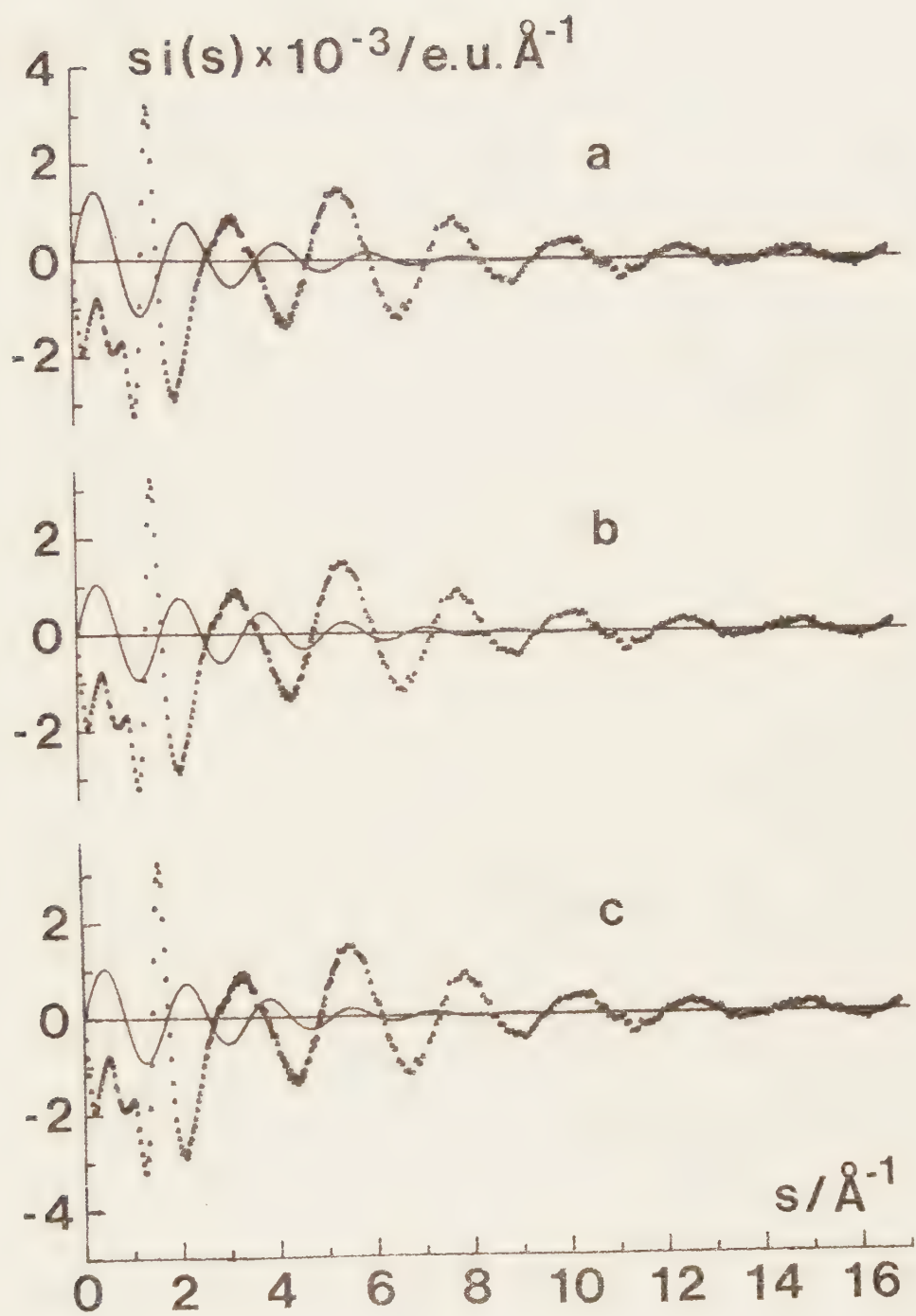
Fig. 5. $\underline{D}(\underline{r}) - 4\pi r^2 \rho_O$ functions for the HgX_4^{2-} solutions (solid lines) compared with sums of calculated peak shapes (dashed lines). The differences are shown by dashed-dotted lines.

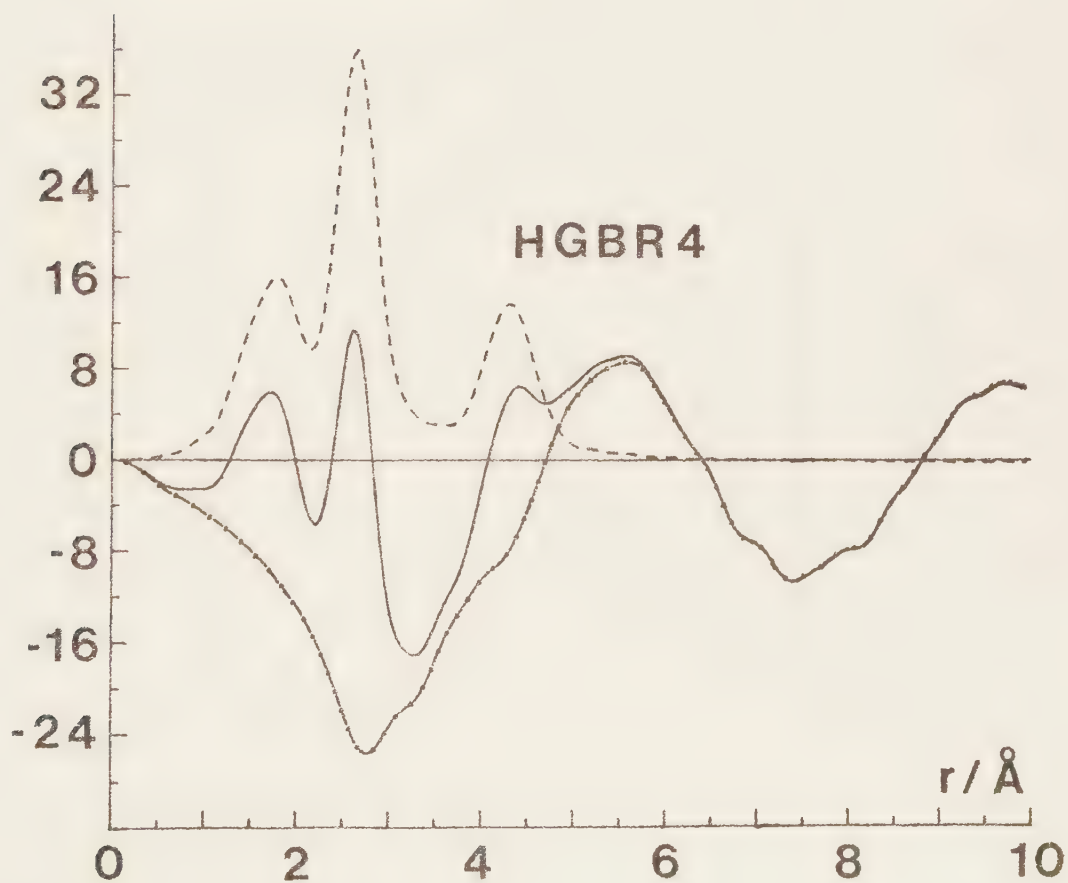
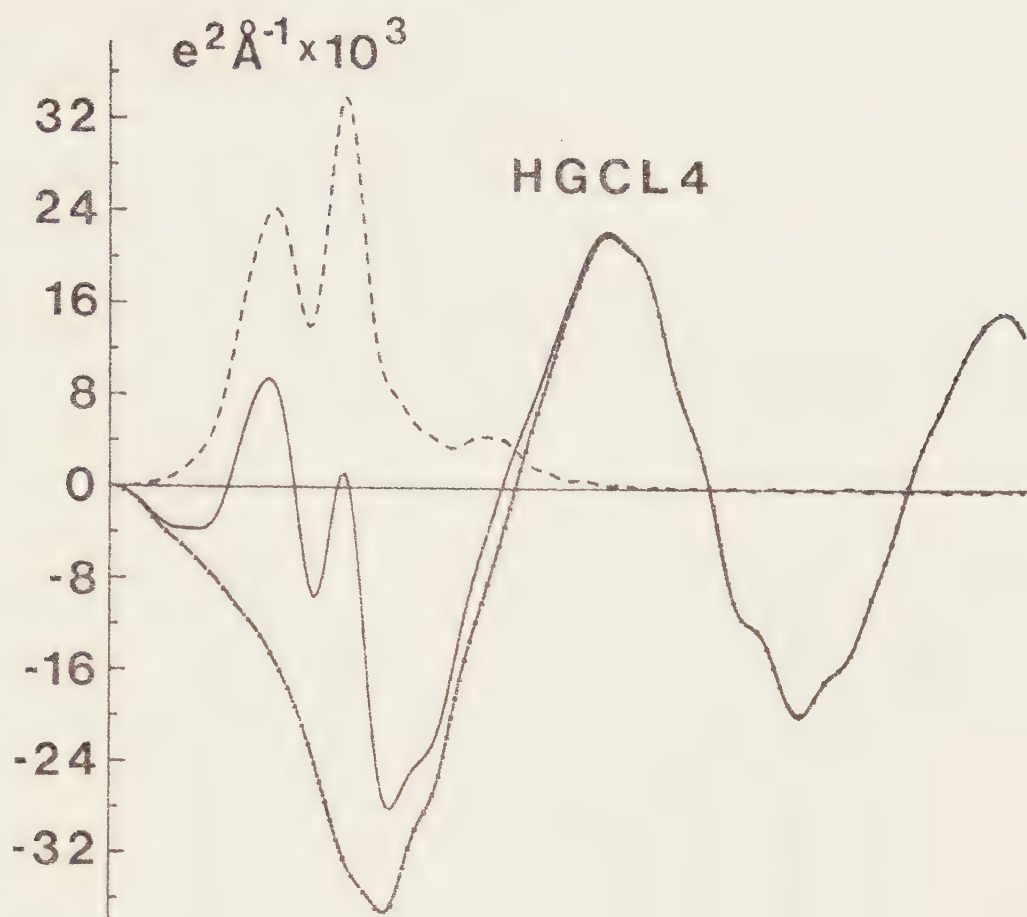
Fig. 6. Reduced intensities multiplied by $\underline{s}$ for investigated HgX_4^{2-} solutions, plotted according to the scheme given in Fig. 3.

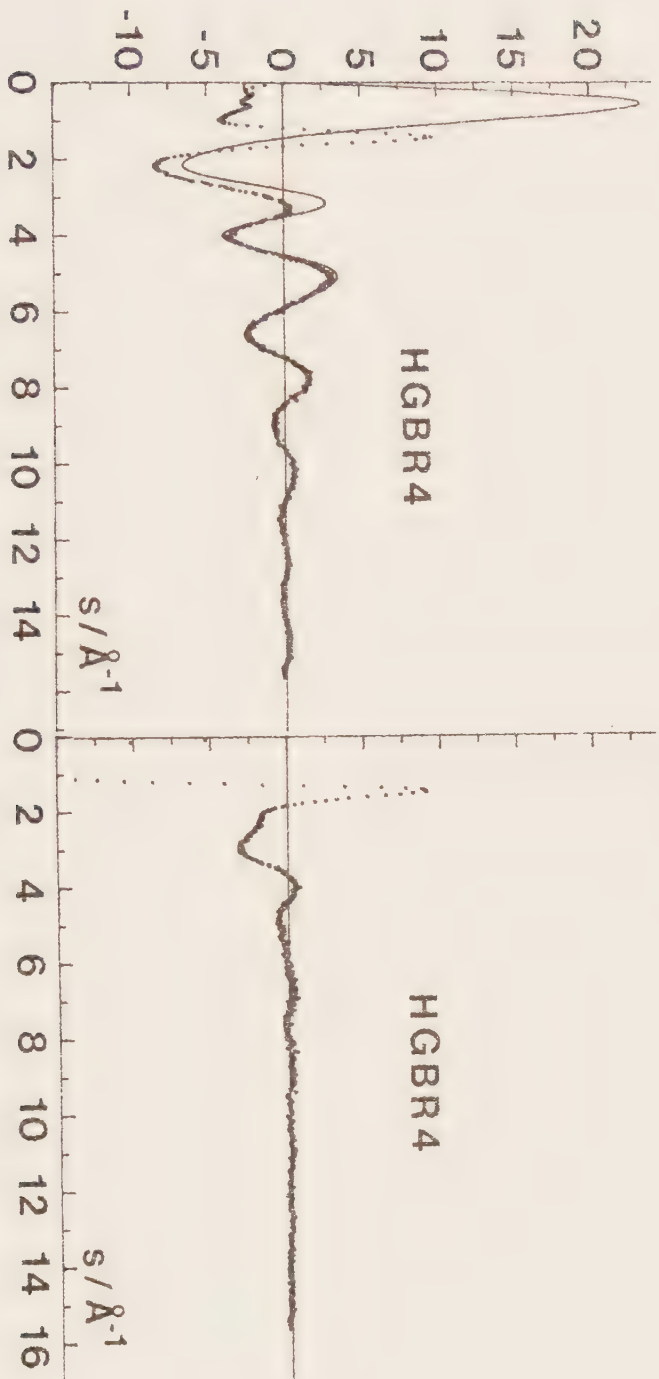
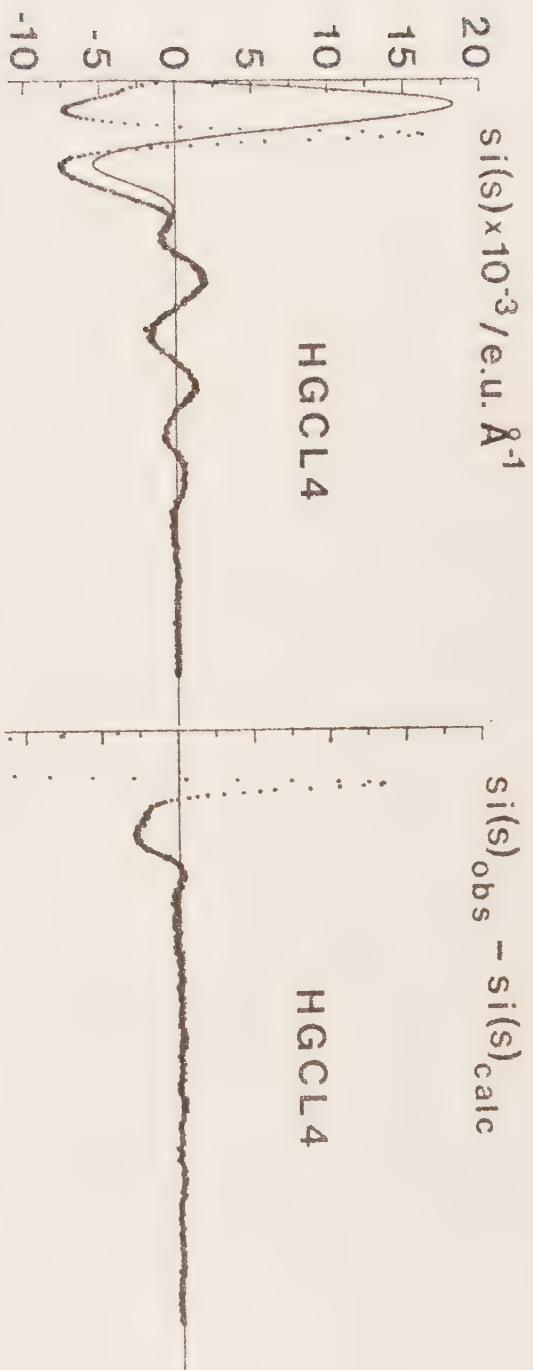












Received:

Other sheets: 3

Correspondence and proofs should be sent to:

Fil.kand. Ingmar Persson, Oorganisk kemi 1, Kemicentrum,
Lunds Universitet, Box 740, S-220 07 Lund 7, Sverige

Running titles: Persson, Iverfeldt and Ahrland

Metal Thiocyanate Complexes in DMSO

An X-Ray Diffraction and Raman Study of Mercury(II), Cadmium(II) and Zinc(II) Thiocyanate Complexes in Dimethylsulfoxide Solution.

INGMAR PERSSON^a, ÅKE IVERFELDT^b and STEN AHRLAND^a

^a Inorganic Chemistry, Chemical Center, University of Lund,
P.O. Box 740, S-220 07 Lund 7, Sweden

^b Department of Inorganic Chemistry, University of Gothenburg,
Chalmers Institute of Technology, S-412 96 Göteborg, Sweden

X-ray diffraction and raman studies of mercury(II), cadmium(II) and zinc(II) thiocyanate complexes in dimethylsulfoxide (DMSO) solution have resulted in the elucidation of the structures of $\text{Hg}(\text{SCN})_2$, $\text{Hg}(\text{SCN})_3^-$, $\text{Hg}(\text{SCN})_4^{2-}$ and $\text{Zn}(\text{NCS})_4^{2-}$.

In the complexes of the soft acceptor Hg^{2+} , the thiocyanate ions are coordinated via S. In $\text{Hg}(\text{SCN})_2$, the two Hg-S bonds are not colinear. This complex is also rather strongly solvated, most likely by 4 DMSO, via O. A tetrahedral arrangement is found already in $\text{Hg}(\text{SCN})_3^-$, with a DMSO completing the tetrahedron. The saturated complex $\text{Hg}(\text{SCN})_4^{2-}$ is regularly tetrahedral. The Hg-S distances increase, and the Hg-S stretching frequencies decrease, as more SCN^- are coordinated, indicating that the strength of the bonds Hg-S decrease in that order. The angle Hg-S-C is in all these complexes $\approx 107^\circ$. The complex HgSCN^+ is completely disproportionated at the high mercury(II) concentrations used in the structure determinations. Naturally, the thiocyanate complexes behave rather similarly to the analogous halide complexes investigated previously.

The complexes $\text{Cd}(\text{SCN})_2$ and $\text{Cd}(\text{SCN})_3^-$ are no doubt S-coordinated in DMSO while in water N-coordination presumably occurs. Such switches seem natural for an acceptor like Cd^{2+} , on the borderline between hard and soft. In the complex $\text{Zn}(\text{NCS})_4^{2-}$ of the hard acceptor Zn^{2+} , the thiocyanate ions are coordinated via N in a regular tetrahedral arrangement, with an angle Zn-N-C = 180° .

In the present study, the structures of thiocyanate complexes formed by mercury(II), cadmium(II) and zinc(II) in DMSO solution have been determined, primarily by x-ray diffraction measurements.

Mercury(II) forms a series of mononuclear complexes $\text{Hg}(\text{SCN})_j^{2-j}$, $j=1-4$. At least in the dilute solutions (mercury concentration

$C_M \leq 20 \text{ mM}$) used in the stability measurements, the consecutive steps are well separated except for the third one.¹ At the ligand number $\bar{n} = \underline{j}$, the complex $\text{Hg}(\text{SCN})_j^{2-j}$ completely predominates in solution, except for $\text{Hg}(\text{SCN})_3^-$ which at $\bar{n} = 3$ reaches a maximum share of only 50%. Such a solution also contains large amounts of $\text{Hg}(\text{SCN})_2$ and $\text{Hg}(\text{SCN})_4^{2-}$ which would seriously impair the structure determination. The conditions would thus be less favourable than in the mercury(II) halide systems where all steps are well separated in DMSO.¹ Fortunately enough, however, the relative stability of $\text{Hg}(\text{SCN})_3^-$ increases very much with C_M . At the fairly high value of C_M ($= 0.8 \text{ M}$) that has been used in the diffraction measurements at $\bar{n} = 3$, $\text{Hg}(\text{SCN})_3^-$ is in fact completely predominating, as shown by the raman spectrum of the solution, cf. below.

In DMSO, the fairly high concentrations necessary for a successful structure determination can be reached for all the complexes $\text{Hg}(\text{SCN})_j^{2-j}$, $j = 2-4$. The neutral complex $\text{Hg}(\text{SCN})_2$, slightly soluble in water, is readily soluble in DMSO. Like in the study of the halide complexes, the extra amounts of ligand necessary to form the higher complexes are added as the sodium salt.²³ With Na^+ as counterion, high concentration of both $\text{Hg}(\text{SCN})_3^-$ and $\text{Hg}(\text{SCN})_4^{2-}$ can be reached. The conditions for the structure determination of these complexes are thus very favourable.

For the first step the situation is, on the other hand, less favourable. In the halide systems, the structures of the complexes HgX^+ cannot be determined by x-ray diffraction as solutions concentrated enough disproportionate extensively into Hg^{2+} and HgX_2 in the case of chloride and bromide, and into HgI_2 and the dinuclear Hg_2I^{3+} in the case of iodide.^{2, 4} As will be shown below, a disproportionation analogous to that found for chloride and bromide occurs also in the thiocyanate system as the mercury(II) concentration is increased.

The soft Hg^{2+} should coordinate the ambident ligand SCN^- by its softer donor atom S. Such a coordination has also been

inferred in aqueous solution from measurements of the intensities of the band in infrared due to C-N stretching.⁵ Also raman measurements of the shift of the C-S stretching frequency in $\text{Hg}(\text{SCN})_4^{2-}$ relative to free SCN^- leads to the same conclusion.⁶ The frequency decreases considerably, as expected for a coordination via S. For the solids $\text{Hg}(\text{SCN})_2$ and $\text{K}_2\text{Hg}(\text{SCN})_4$, exactly the same downward shift of the C-S frequency has been observed, indicating the same coordination.⁷ Later the Hg-S coordination of the entities $\text{Hg}(\text{SCN})_2$ and $\text{Hg}(\text{SCN})_4^{2-}$ has been confirmed by complete structure determinations.⁸⁻¹¹

The cadmium(II) thiocyanate complexes formed in DMSO are fairly weak.¹² At the highest concentration of ligand used, $\bar{n}$ reaches ≈ 2.3 , implying a beginning formation of the third complex. For the cadmium(II)halide systems, the thermodynamics clearly indicate a switch of coordination at the formation of the second complex in DMSO, implying that the original octahedral configuration is changed into a tetrahedral one. In the thiocyanate systems such a switch does not occur. Even the third complex is presumably still octahedral.¹²

The mode of coordination of SCN^- to Cd^{2+} in solution is not well known. Being an acceptor on the borderline between soft and hard, Cd^{2+} might well act differently in different cases. Also, as the affinities to S and N presumably do not differ very much, polynuclear complexes with thiocyanate bridges might easily be formed.

The infrared spectra of aqueous cadmium(II) thiocyanate solutions suggest that both mononuclear and bridged polynuclear complexes are formed.⁵ Any conclusion about the mode of coordination in the mononuclear complexes is not drawn, however, though the frequency shift of the C-N bond relative to free SCN^- speaks very much in favour of a coordination via N. In crystalline $\text{Cd}(\text{SCN})_2$, the central ion octahedrally coordinates 2 N and 4 S. The thiocyanate ions thus act as

bridges but the bond lengths clearly show that the Cd-N interactions are by far the stronger ones.¹³ An example of pure N-coordination is provided by $\text{Cd}(\text{NCS})_2(\text{dpt})$ (dpt = di-(3 aminopropyl)amine).¹⁴ The structure of this compound is composed of discrete molecules. Besides the tridentate amine, two thiocyanate ions are coordinated to the central ion via their N atoms, completing a square pyramide. Especially the N atom of the apical thiocyanate ion is very tightly bonded. In this compound, the S atoms do not at all participate in the coordination of Cd^{2+} .

In other thiocyanate complexes, however, the Cd-S interactions are no doubt the stronger ones. This is e.g. the case in $\text{Cd}(\text{SCN})_2(\text{etu})_2$ (etu = ethylenethiourea), a compound where the cadmium atoms are joined by double thiocyanate bridges.¹⁵

In the present investigation, the structures of the complexes present in a cadmium thiocyanate DMSO solution of $\bar{n} = 2.3$ have been determined by x-ray diffraction. Subsidiary information has been obtained from the raman spectrum of this solution, and from the spectrum of crystalline $\text{Cd}(\text{SCN})_2$.

Zinc(II) coordinates thiocyanate fairly strongly in DMSO. Finally $\text{Zn}(\text{NCS})_4^{2-}$ is formed, most probably of tetrahedral configuration. The thermodynamics indicates that the switch from the octahedral structure of the solvate $\text{Zn}(\text{DMSO})_6^{2+}$ occurs already as the second complex is formed.¹⁶

The hard Zn^{2+} prefers hard donors, and therefore coordinates SCN^- by its harder donor atom N. This mode of coordination has been established in aqueous solution, from measurements of the intensity of the C-N bond.^{5, 17} These measurements also show, however, that the Zn-N interaction is quite weak in aqueous solution. This is also compatible with the fairly low stabilities of the zinc thiocyanate complexes in this solvent.¹⁸ Also the increase of the C-S stretching frequency found for the complexes relative to free SCN^- by raman measure-

ments proves that N-coordination takes place.⁵ The same upward shift of this frequency has also been observed for solid zinc thiocyanate complexes.⁷ In other complexes, however, thiocyanate bridges are formed implying that also S-coordination occurs.¹⁹ This is the case e.g. in $\text{Zn}(\text{NCS})_2$, where zinc otherwise would not be able to attain a sufficiently high coordination number. In this compound, the zinc atoms are all tetrahedrally coordinated, surprisingly either by 4 N or by 4 S atoms.²⁰

In the present investigation, the structure of the complex $\text{Zn}(\text{NCS})_4^{2-}$ has been determined in DMSO solution. Also the raman spectrum of this solution, and of solid $\text{Zn}(\text{NCS})_2$, have been recorded.

EXPERIMENTAL

Preparation of solutions. The solutions investigated were prepared by dissolving in DMSO appropriate amounts of zinc(II), cadmium(II), mercury(II) and sodium thiocyanate, and, in the case of the solution HgSCNl , solvated mercury(II) perchlorate, $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$.²¹ The DMSO was purified as described previously.²² The composition of the solutions is given in Table 1.

The distribution of the consecutive complexes as a function of the free thiocyanate concentration, as calculated from the stability constants determined, is given in Fig. 1. In this Figure, the compositions of the present solutions are also indicated.

X-ray data collection. The x-ray scattering of MoK_α -radiation ($\lambda = 0.71069 \text{ \AA}$) was measured from the free surface of the solutions as described elsewhere.^{23, 24} The apparatus and procedure has also been described previously.²⁵ The measurements were carried out at $25 \pm 1^\circ \text{C}$.

Raman measurements. The Raman spectra were recorded in the range 1500 to 100 cm^{-1} with a Cary 82 argon ion laser spectrophotometer as described previously.²¹ The spectral measurements were performed at room temperature.

X-RAY DATA TREATMENT

The data reduction was performed as described previously.²⁶ The experimental intensities were normalized to a stoichiometric unit of volume containing one metal atom, $\underline{V}$. From the reduced intensity curves, $\underline{i}_{\text{obs}}(\underline{s})$, multiplied by $\underline{s}$, the electronic radial distribution functions (RDF), $\underline{D}(\underline{r}) - 4\pi \underline{r}^2 \rho_0$, were obtained by a Fourier transformation. The same modification function as before was used.²⁶ The least squares refinements of distinct intramolecular interactions were performed minimizing the sum $\sum_{\underline{s}(\text{min})}^{\underline{s}(\text{max})} \underline{w}(\underline{s}) (\underline{i}_{\text{obs}}(\underline{s}) - \underline{i}_{\text{calc}}(\underline{s}))^2$, according to the same procedure as before.^{25, 26} In these calculations fixed values were introduced for the interatomic distances within the species DMSO , ClO_4^- and SCN^- . These were taken from structure determinations of liquid DMSO ⁴ and crystalline structures^{27, 28} of alkali salts, respectively. The RDF's are given in Fig. 2 and the intensity functions in Fig. 3. In these figures the experimental curves are also compared with the intensities calculated from the parameters determined.

RESULTS

Raman measurements. The important raman frequencies found for the solutions investigated, and for the solid thiocyanates $\text{M}(\text{SCN})_2$, $\text{M} = \text{Zn}, \text{Cd}, \text{and Hg}$, are listed in Table 2. For comparison, the bands of the free thiocyanate ion, present in ammonium thiocyanate solution, and in solid NaSCN , have also been measured.

For solid $\text{Hg}(\text{SCN})_2$, the earlier results indicating S-coordination are confirmed. The S-C frequency shifts downwards, the

C-N frequency upwards, though not very much. For solid $\text{Cd}(\text{NCS})_2$, on the other hand, both frequencies shift upwards, in the case of C-N quite considerably. This indicates that the strongest coordination is via N, in conformity with the result of the structure investigation.¹³ For solid $\text{Zn}(\text{NCS})_2$, the indications of N-coordination are even stronger. Evidently, in the structure of this compound,²⁰ cf. above, the interactions between Zn and N are much stronger than those between Zn and S.

As to the DMSO solutions, the S-C stretch frequency is observed only for $\text{Zn}(\text{NCS})_4^{2-}$ where the large upward shift confirms that the coordination takes place via N, as expected. The downward shifts certainly taking place in the S-coordinated mercury(II) complexes cause their S-C bonds to disappear in the intense symmetric S-C stretch frequency of DMSO. The circumstance that no S-C bond is found for the cadmium solution suggests that also Cd^{2+} is coordinated via S. The mode of coordination in DMSO would thus be different from that in aqueous solution, or solid $\text{Cd}(\text{SCN})_2$. Also the small shift in the C-N frequency in DMSO suggests a S-coordination in this solvent.

The very intense peaks found around 250 cm^{-1} for the mercury(II) solutions have been assigned to the Hg-S stretching mode. Between the solutions of $\frac{C_L}{C_M} = 2, 3$ and 4, the frequency decreases with increasing number of ligands coordinated, as is also found for the corresponding halide complexes.² The differences between the solution of $\frac{C_L}{C_M} = 1$ and 2 is very small, however, Table 2. In the solution of $\frac{C_L}{C_M} = 1$, bands characteristic of the solvate $\text{Hg}(\text{DMSO})_6^{2+}$ moreover appear, viz. the Hg-O bending and stretching frequencies at 210 and 425 cm^{-1} , respectively.²¹ Obviously, the complex HgSCN^+ predominating in dilute solutions disproportionates as $\frac{C_M}{C_L}$ increases, according to $2\text{HgSCN}(\text{DMSO})_6^+ + n\text{DMSO} \rightleftharpoons \text{Hg}(\text{DMSO})_6^{2+} + \text{Hg}(\text{SCN})_2(\text{DMSO})_9$. The pattern would thus be the same as for HgCl^+ and HgBr^+ , though the solvation of the complexes might well be different.⁴

The intensity of the band due to $\text{Hg}(\text{SCN})_2$ at 270 cm^{-1} is proportional to $\underline{C}_M$ in the range $0.25 \leq \underline{C}_M \leq 0.8\text{ M}$ and the intensity found for the solution of $\underline{C}_M = 0.5\text{ M}$ is moreover the same as that observed for a genuine $\text{Hg}(\text{SCN})_2$ solution of $\underline{C}_M = 0.25\text{ M}$. Consequently, the disproportionation is complete in the range stated. For values of $\underline{C}_M < 0.25\text{ M}$, the band due to $\text{Hg}(\text{SCN})_2$ becomes less intense than warranted by the decrease of $\underline{C}_M$, until it completely disappears at $\underline{C}_M \approx 0.05\text{ M}$. At that concentration, the repropportionation to HgSCN^+ is evidently complete. No band that can be assigned to this complex appears, however. Like the halide complexes HgX^+ , HgSCN^+ is seemingly raman inactive.⁴

In solid $\text{Hg}(\text{SCN})_2$, $\underline{\nu}_1(\text{Hg-S})$ is observed at a slightly higher frequency than in DMSO solution, indicating a somewhat stronger bond in the crystalline phase, Table 2. This seems natural, considering that the bond should be weakened in solution on account of the solvation.

The spectrum of $\text{Hg}(\text{SCN})_2$ solution has a very weak band at 318 cm^{-1} which is assigned to the vibration $\underline{\nu}_3(\text{Hg-S})$. The complex would thus be bent. This is certainly to be expected if it is still fairly strongly solvated. In the solid where the Hg-S bonds are colinear,⁸ this band is neither expected, nor observed.

The spectrum of the solution HGSCN_3 shows only one sharp and intense peak, at 241 cm^{-1} , which should evidently be assigned to $\text{Hg}(\text{SCN})_3^-$, Table 2. No traces of the bands due to $\text{Hg}(\text{SCN})_2$ or $\text{Hg}(\text{SCN})_4^{2-}$ are observed, in spite of the fact that each of these complexes account for $\approx 25\%$ of the total $\underline{C}_M$ in the dilute solutions used in the stability measurements, Fig. 1. Evidently, the partial disproportionation of $\text{Hg}(\text{SCN})_3^-$ taking place under these conditions does not occur in the concentrated solutions used in the structure determinations. In this respect, the behaviour of $\text{Hg}(\text{SCN})_3^-$ is just the opposite to that of HgSCN^+ .

For the cadmium(II) solution, no band appears that can be assigned to the Cd-S bond. In solid $\text{Cd}(\text{SCN})_2$, the Cd-N stretch is at the low wavenumber 202 cm^{-1} , much lower than Hg-S, in spite of the lighter donor atom. This confirms that the Cd-N bond is a fairly weak one. The bond Zn-N is much stronger, in both the tetrahedral structures investigated here, viz. $\text{Zn}(\text{NCS})_4^{2-}$ in DMSO, and solid $\text{Zn}(\text{NCS})_2$. In both instances, $\nu_1(\text{Zn-N}) = 240\text{ cm}^{-1}$, i.e. much higher than $\nu_1(\text{Cd-N})$.

Diffraction measurements. For all the solutions investigated, the RDF's have a peak at $\approx 1.7\text{ \AA}$, due to the S-O and S-C distances in DMSO. In the solution HgSCN1, Cl-O distances of $1.43\text{ \AA}$ in ClO_4^- also contribute to the diffraction in this region. The large and broad peak around $5.5\text{ \AA}$ is due to interactions between DMSO molecules, as evident from the RDF of pure DMSO, Fig. 2. As no data exist about the intermolecular structure of DMSO, this peak is not accounted for in the refinements of the structures of the complexes present.

For the mercury(II) thiocyanate solutions, the sharp peak at 2.4 to $2.5\text{ \AA}$ corresponds to the Hg-S bond distance. In the solutions HGSCN4 and HGSCN3 shoulders are observed at ≈ 4.3 and $4.0\text{ \AA}$, respectively, due to the interligand S-S distances. For the solution HGSCN2 no such shoulder can be discerned. In $\text{Hg}(\text{SCN})_2$, the two S atoms are presumably so far apart that the corresponding diffraction disappears in the broad DMSO peak; moreover the intensity of this interaction is low, as it involves only one S-S distance.

The RDF of HGSCN2 shows a small but distinct peak at $3.7\text{ \AA}$ which most probably is due to the interaction Hg-S_D between the central ion and the S atoms of coordinated DMSO molecules. The long distance indicates that DMSO is coordinated via oxygen, as in $\text{Hg}(\text{DMSO})_6^{2+}$. The corresponding Hg-O bond length would be $2.7\text{ \AA}$. The solvate bonds are thus quite weak in comparison with those in $\text{Hg}(\text{DMSO})_6^{2+}$ where the Hg-O bond length is only $2.39\text{ \AA}$. Also in the RDF of HGSCN3 an interaction Hg-S_D can be clearly discerned, at $\approx 3.7\text{ \AA}$.

As the bond lengths Hg-O in $\text{Hg}(\text{DMSO})_6^{2+}$ and Hg-S in $\text{Hg}(\text{SCN})_2$ are about the same, the peak due to the coordinate bonds in the RDF of the disproportionated solution HGSCN1 should be in the same position as for HGSCN2. This is also the case, though the peak is less intense in HGSCN1, due to the much lower concentration of $\text{Hg}(\text{SCN})_2$ and to the low scattering factor of the oxygen atom in the Hg-O interaction. Also in this RDF a diffraction due to the solvation of $\text{Hg}(\text{SCN})_2$ can be discerned.

Only in the RDF of HGSCN4a, i.e. the most concentrated solution of $\text{Hg}(\text{SCN})_4^{2-}$, the Hg-C distances are immediately discerned at ≈ 3.4 Å. Also for HGSCN3 and HGSCN2, these interactions are found in the refinements, however.

Only in the RDF of HGSCN3, the Hg-N distances are immediately discerned as a shoulder at 4.3 Å. In the case of HGSCN4, this shoulder evidently merges with that due to the S-S interactions.

In the case of HGSCN1, completely disproportionated into 0.25 M $\text{Hg}(\text{DMSO})_6^{2+}$ and 0.25 M $\text{Hg}(\text{SCN})_2$, no refinement of the parameters has been performed. The calculated curves in Figs. 2 and 3 have been obtained by introducing the parameters determined earlier for $\text{Hg}(\text{DMSO})_6^{2+}$ and presently for $\text{Hg}(\text{SCN})_2$.

For the other mercury(II) solutions, the results of the refinements are given in Table 3. For those parameters that are possible to refine, the standard deviations are given within paranthesis. These of course do not include systematic errors which may be of at least the same order of magnitude. The Hg-S distances can be refined for all solutions, and Hg-C (though with a much larger error) for all except HGSCN4b. The M-N distances are calculated from the known structure²⁸ of SCN^- and the angles Hg-S-C determined here, Table 4. For the most strongly solvated complex $\text{Hg}(\text{SCN})_2$ (solution HGSCN2) also the parameters pertaining to the solvation (distances Hg-S_D; number of DMSO coordinated, n) can be refined. Only

in the case of HGSCN4a, the S-S interactions are prominent enough to be refined. No further refinement is possible for the S-S interaction found at 4.0 Å in the RDF of HGSCN3. This value fits well with a tetrahedral arrangement of the S atoms, however. As moreover a Hg-S_D interaction is indicated in the RDF, one DMSO has been introduced in the fourth tetrahedral position. For this DMSO, a Hg-O distance of 2.7 Å has been calculated from the observed $\underline{d}(\text{Hg-S}_D) = 3.7$ Å, on the assumption that the angle Hg-O-S is the same as in $\text{Hg}(\text{DMSO})_6^{2+}$, viz. 120°.

In the RDF of the cadmium(II) thiocyanate solution CDSCN2, a peak appears at 2.6 Å. This distance fits to a Cd-S octahedral bond. Such bonds are generally in the range^{15,29,30} 2.64 to 2.66 Å. For a Cd-N coordination, on the other hand, a bond length ≈ 2.3 Å would be expected as the covalent radius of N is 0.34 Å shorter than that of S.³¹ Also the interaction Cd-S in DMSO is clearly seen in the RDF, at ≈ 3.4 Å.

For the refinements, a structural model has been assumed where on the average 2.3 SCN are coordinated per Cd, as indicated by the stability measurements. The complexes present are thus mainly $\text{Cd}(\text{SCN})_2$ and $\text{Cd}(\text{SCN})_3^-$, Fig. 1. The thermodynamics further indicates that these complexes are still octahedral.¹² Therefore 3.7 DMSO have been introduced, coordinated via O at the same distance as in $\text{Cd}(\text{DMSO})_6^{2+}$. Only the Cd-S distance can be refined. The distance M-C has been calculated, assuming an angle M-S-C = 107°.

In the RDF of the zinc(II) solution ZNSCN4, the Zn-N interaction of the tetrahedral $\text{Zn}(\text{NCS})_4^{2+}$ is expected at 1.9 Å.^{32,33} This diffraction is not intense enough to be observed, Fig. 2. The broad DMSO band around 5.5 Å has a marked shoulder at ≈ 4.7 Å, however. On the reasonable assumption that the Zn-N bond is colinear with the SCN⁻ ion, as is found in solid complexes²⁸ this distance would be a reasonable one for Zn-S. The corresponding Zn-N distance would then be ≈ 1.9 Å, i.e. as expected. The Zn-S distance has been refined, and the result is listed in Table 3.

DISCUSSION

Mercury(II) thiocyanate. The raman and x-ray diffraction studies concur that HgSCN^+ is completely disproportionated in DMSO solutions concentrated enough for structural studies. On the other hand, $\text{Hg}(\text{SCN})_3^-$ which is extensively disproportionated in dilute solutions is completely predominating in concentrated solution of $\bar{n} \approx \underline{C}_L/\underline{C}_M = 3$. The structures of the complexes $\text{Hg}(\text{SCN})_j^{2-j}$, $j = 2-4$, can therefore be determined. They are all, as expected, S-coordinated. In $\text{Hg}(\text{SCN})_4^{2-}$, the S-atoms are in a regular tetrahedron. The ratio $\underline{d}(\text{Hg-S})/\underline{d}(\text{S-S})$ found is 0.617(3), very close to the theoretical value of 0.612. Structurally, $\text{Hg}(\text{SCN})_4^{2-}$ is thus analogous to the halide complexes HgX_4^{2-} as is certainly expected. Also $\text{Hg}(\text{SCN})_3^-$ is approximately tetrahedral, with a DMSO in the fourth position. This structure is very similar to that found³ for HgI_3^- . In HgBr_3^- , the trigonal pyramide is already flattened considerably and in HgCl_3^- , the arrangement is trigonally planar² (presumably with two DMSO completing a bipyramide).

Like HgI_2 , HgBr_2 and, presumably, also HgCl_2 , the complex $\text{Hg}(\text{SCN})_2$ is bent in DMSO. In the case of the two latter complexes, the Cl-Cl and S-S diffractions are not intense enough, however, to allow the determination of the deviations from linearity. The neutral complexes are rather extensively solvated, presumably by four DMSO. To judge from the Hg-O bond lengths found generally, $\approx 2.6 \text{ \AA}$, the solvate bonds are of much the same strength in $\text{Hg}(\text{SCN})_2$ as in the halide complexes.² As might be expected, the bonds are considerably longer, and hence weaker, than in the solvate²¹ $\text{Hg}(\text{DMSO})_6$ where $\underline{d}(\text{Hg-O}) = 2.39 \text{ \AA}$. In the case of the halides, the large difference in solvate bond strength between HgX_2 and $\text{Hg}(\text{DMSO})_6^{2+}$ has also been directly proved by determinations of the respective solvation enthalpies.³⁴

To judge from the entropy changes $\underline{\Delta S}_j^0$ found for the consecutive steps in the systems discussed, $\text{Hg}(\text{SCN})_2$ should be more strongly solvated than the halide complexes¹ HgX_2 . In the

concentrated solution used in the present structure investigation, this is seemingly not the case, however. That such a difference exists between solutions of so very different concentrations ($C_M \leq 20$ mM in the thermodynamic measurements) is of course not surprising. Similar differences are of course implied in the destabilization of HgSCN^+ , and the stabilization of $\text{Hg}(\text{SCN})_3^-$ already discussed.

An important reason for these changes is no doubt that the structure of the solvent changes drastically with C_M . At sufficiently high concentrations, the unstructured bulk solvent is bound to disappear.⁴ Consequently, the huge entropy gains accompanying the break-up of an ordered solvate in dilute solution will also largely disappear. This means that complexes which are highly entropy stabilized in dilute solution will be destabilized with increasing C_M , as is in fact found for both HgSCN^+ and all the halide complexes HgX^+ .

The bond length Hg-S increases with the number of ligands coordinated, implying a weakening of the bond in the same order, Table 4. This weakening is also reflected in the decrease of the $\nu_1(\text{Hg-S})$ frequency, Table 4. In all the halide systems, completely analogous changes of bond length and bond strength also occur.² Naturally enough, the bonds become weaker as the bonding capacity of the central ion has to be divided between more ligands.

The bond length Hg-S in $\text{Hg}(\text{SCN})_4^{2-}$ is close to those found in solids containing this entity.⁹⁻¹¹

The angle Hg-S-C is in all the complexes $\approx 107^\circ$, Table 2. An angle of this magnitude is the rule for thiocyanate complexes coordinated via S. For complexes coordinated via N, on the other hand, the angle M-N-C is generally 180° .²⁸

As to cadmium(II), the present results confirm the inference that for this borderline acceptor small changes of the con-

ditions are sufficient to change the coordination of an ambident ligand as SCN^- . In DMSO, S-coordination no doubt prevails while in aqueous solution the opposite is presumably the case. In solids, both modes evidently exist, and bridged compounds where they are used simultaneously are, as might be expected, common.

For zinc(II), the preference for N over S is evident. This does not preclude however, that in solids S-coordination often occurs in order to create a favourable coordination polyhedron.

Acknowledgements: Our sincere thanks are due to Professor Oliver Lingqvist whose continued interest has been most important for our progress. The financial support given by The Swedish Natural Science Research Council is gratefully acknowledged.

REFERENCES

1. Ahrland, S., Persson, I. and Portanova, R. To be published.
2. Sandström, M. Acta Chem. Scand. A32 (1978) 627
3. Gaizer, F. and Johansson, G. Acta Chem. Scand. 22 (1968) 3013
4. Ahrland, S., Hansson, E., Iverfeldt, Å. and Persson, I. To be published.
5. Fronæus, S. and Larsson, R. Acta Chem. Scand. 16 (1962) 1447
6. Taylor, K.A., Long, T.V. and Plane, R.A. J. Chem. Phys. 47 (1967) 138
7. Turco, A. and Pecile, C. Nature 191 (1961) 66
8. Beauchamp, A.L. and Goutier, D. Can. J. Chem. 50 (1972) 977
9. Scouloudi, H. Acta Crystallogr. 6 (1953) 651
10. Sakhri, A. and Beauchamp, A.L. Acta Crystallogr. A31 (1975) 409
11. Beauchamp, A.L., Pazdernik, L. and Rivest, R. Acta Crystallogr. B32 (1976) 650
12. Ahrland, S. and Björk, N.O. Acta Chem. Scand. A30 (1976) 249, 257
13. Cannas, M., Carta, G., Cristini, A. and Marongiu, G. J. Chem. Soc. Dalton (1976) 300
14. Cannas, M., Cristini, A. and Marongiu, G. Inorg. Chim. Acta 22 (1977) 232
15. Cavalca, L., Nardelli, M. and Fava, G. Acta Crystallogr. 13 (1960) 125
16. Ahrland, S., Björk, N.O. and Portanova, R. Acta Chem. Scand. A30 (1976) 270
17. Stommen, D.P. and Plane, R.A. J. Chem. Phys. 60 (1974) 2643 and references therein
18. Ahrland, S. and Kullberg, L. Acta Chem. Scand. 25 (1971) 3692
19. Norbury, A.H. In Advanced Inorganic Chemistry and Radiochemistry, Academic Press New York San Francisco London 1975, Vol. 17, p. 333

20. Aslanov, L.A., Ionov, V.M. and Kynev, K. Kristallografiya 21 (1976) 1198
21. Sandström, M., Persson, I. and Arhland, S. Acta Chem. Scand. A32 (1978) 607
22. Arhland, S. and Björk, N.O. Acta Chem. Scand. A28 (1974) 823
23. Johansson, G. Acta Chem. Scand. 20 (1966) 553
24. Johansson, G. Acta Chem. Scand. 22 (1968) 2799
25. Levy, H.A., Danford, M.D. and Narten, A.H. Data Collection and Evaluation with an X-Ray Diffractometer Designed for the Study of Liquid Structure, Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge 1966
26. Sandström, M. and Johansson, G. Acta Chem. Scand. A31 (1977) 132
27. Berglund, B., Thomas, J.O. and Tellgren, R. Acta Crystallogr. B31 (1975) 1842
28. Wells, A.F. Structural Inorganic Chemistry, 4th Ed., Clarendon, Oxford 1975
29. Cavalca, L., Domiano, P., Fava Gasparri, G. and Boldrini, P. Acta Crystallogr. 22 (1967) 878
30. Bigoli, F., Braibanti, A., Pellinghelli, M.A. and Tiripicchio, A. Acta Crystallogr. B28 (1972) 962
31. Pauling, L. General Chemistry, 3rd Ed., W.H. Freeman and Company San Francisco 1970, pp. 195
32. Bigoli, F., Braibanti, A., Pellinghelli, M.A. and Tiripicchio, A. Acta Crystallogr. B29 (1973) 2708
33. Caira, M. and Nassimbeni, L.R. Cryst. Struct. Commun 5 (1976) 309
34. Arhland, S., Kullberg, L. and Portanova, R. Acta Chem. Scand. A32 (1978) 251

Table 1. Concentrations(M) of the solutions investigated by X-ray diffraction. The linear absorption coefficient $\mu(\text{cm}^{-1})$ is calculated for MoK_α -radiation.

Solution	Hg(II)	Cd(II)	Zn(II)	SCN^-	ClO_4^-	Na^+	DMSO	μ
HGSCN1	0.50			0.50	0.50		13.2	16.7
HGSCN2	0.80			1.60			13.0	23.8
HGSCN3	0.80			2.40		0.80	12.1	23.8
HGSCN4a	0.50			2.26		1.16	12.3	16.8
HGSCN4b	0.30			1.37		0.77	13.2	12.0
CDSCN2		0.30		1.35		0.75	13.2	6.0
ZNNCS4			0.30	1.35		0.75	13.2	6.1

Table 2. Raman frequencies observed for the solutions listed in Table 1, 0.5 M NH_4SCN in DMSO, and the solids $\text{Hg}(\text{SCN})_2$, $\text{Cd}(\text{SCN})_2$, $\text{Zn}(\text{SCN})_2$, NaSCN .

Solution	Dominating species	M-N stretch	M-S stretch	S-C stretch ^a	C≡N stretch
NH_4SCN	SCN^-			740	2060
HGSCN1	$\text{Hg}(\text{DMSO})_6^{2+}, \text{Hg}(\text{SCN})_2$		270	<u>b</u>	2133
HGSCN2	$\text{Hg}(\text{SCN})_2$		266 ^c	<u>b</u>	2135
HGSCN3	$\text{Hg}(\text{SCN})_3^-$		241	<u>b</u>	
HGSCN4a	$\text{Hg}(\text{SCN})_4^{2-}$		235	<u>b</u>	2117
CDSCN2	$\text{Cd}(\text{SCN})_2(\text{DMSO})_4$			<u>b</u>	~2090
ZNNCS4	$\text{Zn}(\text{NCS})_4^{2-}$	240		836	2110
Solids	NaSCN			749	2073
	$\text{Hg}(\text{SCN})_2$		274	726	2109+(2061) ^d
	$\text{Cd}(\text{NCS})_2$	202		763	2148
	$\text{Zn}(\text{NCS})_2$	240		790	2163+2182

^a In thiocyanate

^b Hidden by the sym. S-C stretch peak of DMSO

^c A $\nu_3(\text{Hg-S})$ frequency at 318 cm^{-1} is also observed

^d Much weaker than 2109

Table 3. Results of the least-squares refinements on the reduced intensities. The parameters describing atomic interactions are: d =distance ($\text{\AA}$), b =temperaturefactor coefficient ($\text{\AA}^2$) and n =number of distances per metal atom. The refined parameters are those with standard deviations indicated (within parenthesis). The intramolecular intensity contributions from DMSO, SCN^- and ClO_4^- were held constant during the refinements.

Solution		ZNCS4	CDSCN2	HGSCN2	HGSCN3	HGSCN4a	HGSCN4b
M-S	d	4.73(4)	2.634(11)	2.410(2)	2.464(3)	2.547(4)	2.531(7)
	b	0.020	0.010	0.0006(2)	0.0057(4)	0.0037(6)	0.0098(6)
	n	4	2.3	2	3	4	4.1(1)
M-C	d	3.07	3.49	3.287(14)	3.35(4)	3.427(14)	3.40
	b	0.013	0.018	0.005	0.010	0.010	0.012
	n	4	2.3	2	3	4	4
M-N	d	1.93	4.35	4.195	4.24	4.30	4.27
	b	0.007	0.025	0.010	0.018	0.018	0.021
	n	4	2.3	2	3	4	4
S-S	d				4.0	4.127(16)	4.13
	b				0.004	0.004(2)	0.023
	n				3	6	6
M-O	d		2.30	2.655(5)	2.70		
	b		0.012	0.0085(13)	0.012		

Solution	ZNNCS4	CDSCN2	HGSCN2	HGSCN3	HGSCN4a	HGSCN4b
M-S _D	<u>d</u>	3.43	3.656(5)	3.70		
	<u>b</u>	0.020	0.032(3)	0.022		
M-O and M-S _D	<u>n</u>	3.7	3.7(3)	1		

Table 4. Hg-S bond lengths (Å), Hg-S-C angles (degrees) and ν_1 (Hg-S) raman frequencies (cm^{-1}) for mercury(II) thiocyanate complexes in DMSO solution. For comparison, Hg-S bond lengths in solids containing the entities $\text{Hg}(\text{SCN})_2$ and $\text{Hg}(\text{SCN})_4^{2-}$.

Complex	Hg-S (solution)	Hg-S (solids)	Hg-S-C	ν_1 (Hg-S)
$\text{Hg}(\text{SCN})_2$	2.410	2.381 ^b	107	266 ^a
$\text{Hg}(\text{SCN})_3^-$	2.464		107	241
$\text{Hg}(\text{SCN})_4^{2-}$	2.547	2.531 ^c , 2.539 ^d	108	235

^a ν_3 (Hg-S) at 318 cm^{-1}

^b Ref. 8

^c Ref. 10

^d Ref. 11

Text to Figures:

- Fig. 1 Distribution of the zinc(II), cadmium(II) and mercury(II) thiocyanate complexes in diluted DMSO solutions as a function of the free thiocyanate ion concentration. The curves have been calculated from stability constants in 1 M NH_4ClO_4 medium. The compositions of the solutions investigated by X-ray diffraction, calculated on the assumption that the same constants are valid, are indicated by vertical lines.
- Fig. 2 Function $\underline{D}(\underline{r}) - 4\pi \underline{r}^2 \underline{\rho}_0$ (solid lines) compared with sums of calculated peak shapes of the refined model (dashed lines). The parameter values given in Table 3 have been used. The differences are shown by the dashed-dotted lines.
- Fig. 3 Reduced intensities, $\underline{i}(\underline{s})$, multiplied by $\underline{s}$ are shown to the left. Experimental values are denoted by dots (the six first are obtained by extrapolation), values calculated for the refined model by solid lines. The differences, $\underline{s}\hat{i}_{\text{obs}}(\underline{s}) - \underline{s}\hat{i}_{\text{calc}}(\underline{s})$ between experimental and calculated values are shown to the right.

Fig. 1

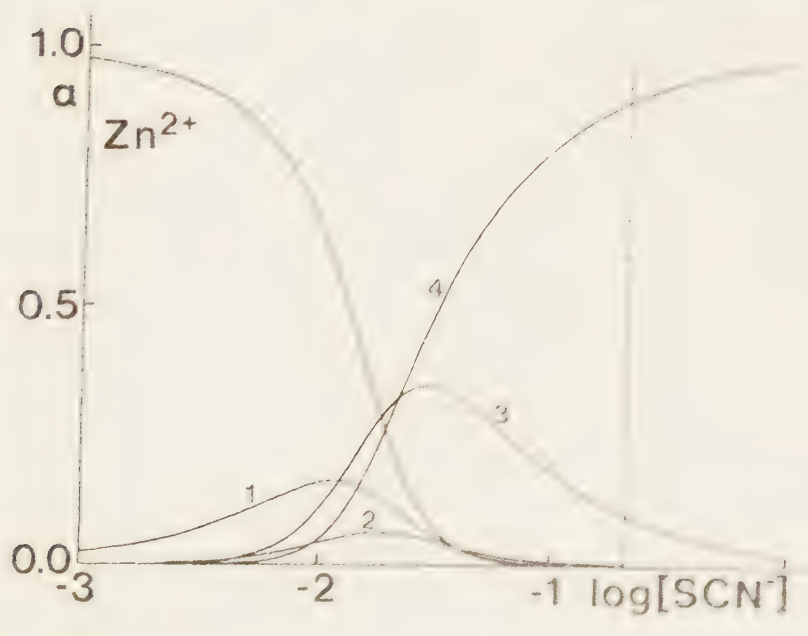
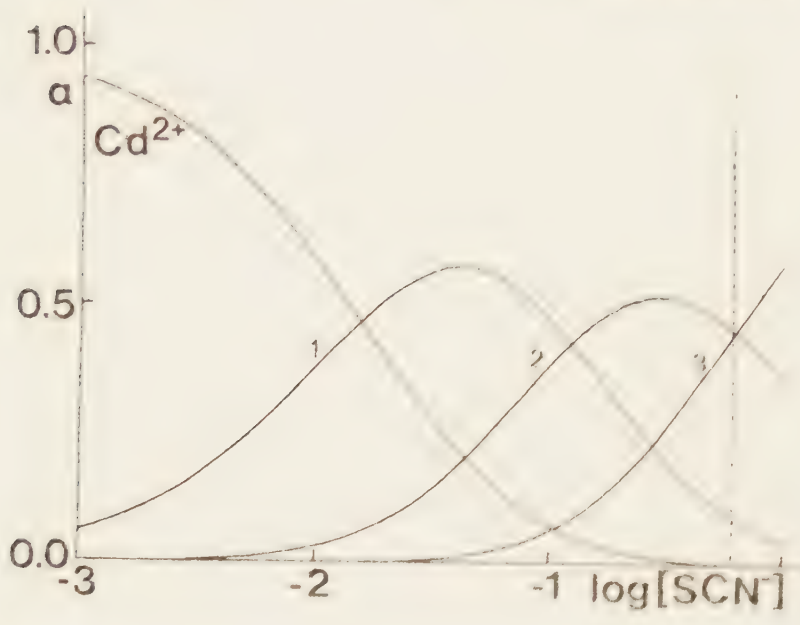
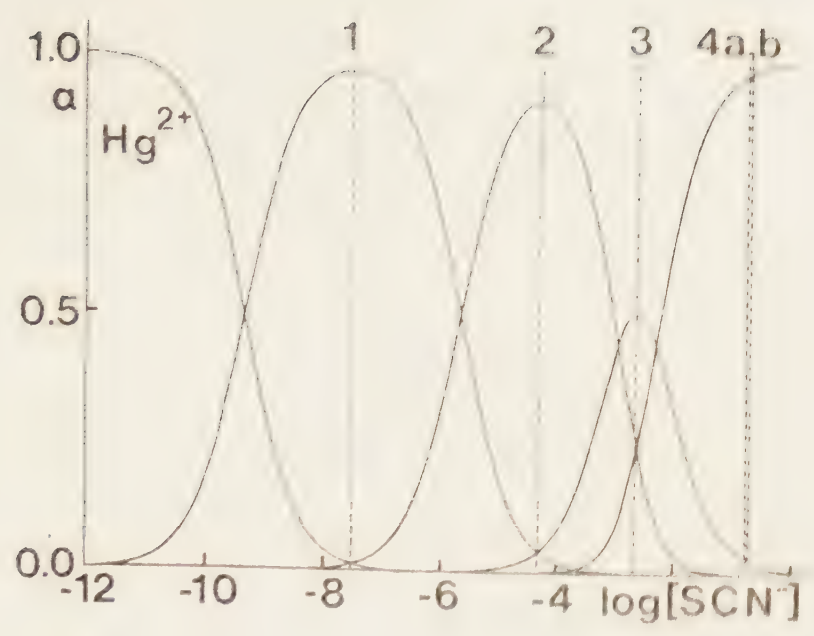


Fig. 2.

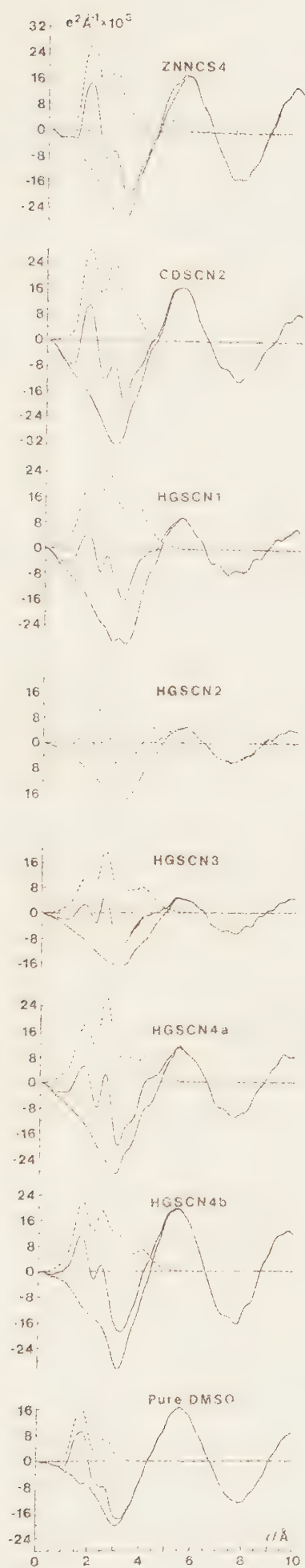


Fig. 3.

